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FOR GAGES IN LIQUID AIRCRAFT METALS

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AUTHORS: H. Kirschik/SL Culp

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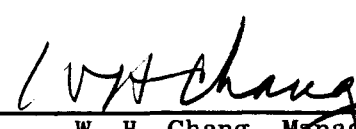
TITLE: BROMINE TRIFLUORIDE METHOD FOR OXYGEN IN LIQUID ALKALI METALS

AUTHORS: Hyman Kirtchik
Siegmond Culp

SUBMITTED BY: Materials Development Laboratory Operation
Advanced Engine & Technology Department
General Electric Company
Evendale, Ohio

SIGNATURES: 

Hyman Kirtchik, Manager
Analytical Chemistry Unit



W. H. Chang, Manager
Materials Applied Research

DATE: March 31, 1965

BROMINE TRIFLUORIDE METHOD FOR OXYGEN
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ABSTRACT

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Potassium is analyzed for oxygen by reacting samples of the metal with bromine trifluoride in a specially constructed monel reaction vessel. The oxygen thus liberated is purged from the reaction cell with helium and mixed with an alkaline solution of sodium anthraquinone β -sulfonate in a modified Brady apparatus. The resulting color change of the reagent solution is measured with a recording spectrophotometer, the change in absorbance being related to the oxygen content by means of a previously prepared calibration curve. Reproducibility of the method is good with coefficients of variation ranging from 1 to 13%.

Essentially, complete oxygen recovery is obtained from potassium bromate synthetic samples, while potassium carbonate additions show the method, as used, to be insensitive to carbonates. The apparatus blanks are in the order of 5-10 μg of O_2 .

Recommendations are given for apparatus changes and more particularly for application of this BrF_3 method to other alkali metals.

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I INTRODUCTION

A. Technical Background

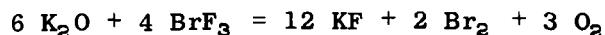
The real effects of potassium corrosion cannot be established with any certainty until the level of impurities, particularly oxygen, can be determined with reasonable accuracy. Various hot-trapping, mass transfer, and corrosion⁽¹⁾ studies have shown that many oxide species may be present; this is particularly true in systems constructed of dissimilar metals. The difficulty with most of the chemical methods of analysis presently employed is that they cannot respond to such oxides or suboxides of the transition metals. In addition, the stoichiometry of the alkali metal oxides present must be known or assumed and various other contaminants may be determined as oxygen.

In an attempt to circumvent these difficulties, the object of this work has been to develop a method which, while remaining specific for oxygen, will respond quantitatively to as many oxide species as possible. At the present time, only the neutron activation method can claim such general applicability and as yet, owing primarily to high container blanks, the precision of the method leaves something to be desired.

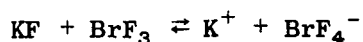
Emeléus and Woolf⁽²⁾ studied the reaction of bromine trifluoride with oxides and some oxyacid salts. It was postulated that the criterion for ready reaction was the formation of a volatile or reagent soluble fluoride of the metal involved. Sheft⁽³⁾ examined the solubility of some metal fluorides in BrF_3 finding the solubility of KF to be $5.38 \pm .03$ gram moles per 100 grams of solution at 70°C . Hoekstra and Katz⁽⁴⁾ used BrF_3 for the quantitative determination of oxygen in metal and metalloid oxides and published a modified periodic table showing the reactivity of bromine trifluoride toward oxides and oxyacid salts. Dupraw and O'Neill⁽⁵⁾ then used a similar method for the direct determination of small amounts of oxygen and nitrogen in titanium and its alloys.

B. Program Phases

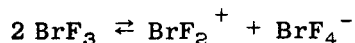
The method employed here in the analysis of alkali metals is based upon the reaction of bromine trifluoride with the subject metal to liberate molecular oxygen which is then measured spectrophotometrically by means of a Brady⁽⁶⁾ apparatus modified according to Silverman and Bradshaw⁽⁷⁾. In the case of K_2O the overall reaction would be:



In accordance with the solvent system of acids and bases, the KF formed can be regarded as a base in BrF_3 since it behaves as a F^- donor in the equilibrium:



Bromine trifluoride possesses the ability to act both as a fluoride ion acceptor or donor:



The alkali metal fluorides are soluble in BrF_3 and essentially completely ionized. The solubility increases as the size of the cation increases.

Quantitative evaluation of the method resulted in a development program which can be subdivided into three phases:

- 1) The design and construction of a system capable of meeting the stringent leak-rate requirements involved and of withstanding BrF_3 and its reaction products.
- 2) Calibration of the oxygen measuring and potassium extrusion sampling systems.
- 3) Determinations of oxygen in potassium and oxygen bearing compounds (bromates and carbonates) and a study of the various analytical parameters involved.

II APPARATUS AND INSTRUMENTATION

The apparatus may be roughly subdivided into three major sections:

1. The Helium Purification System.
2. The Analytical System - including the potassium extruder, KEL-F measuring vessel, reaction chamber, and attendant vacuum systems and cold traps.
3. The Brady Apparatus or oxygen measuring system.

A schematic drawing of the overall apparatus (with the exception of the Brady apparatus) is shown in Figure 1. The various sections of the apparatus are now described in more detail.

A. The Helium Purification System

Commercial tank grade helium is metered into the system by a Matheson Model #8-AF-590 two stage regulator with flow meter. Outlet pressure is set at about 8 psig. Initial purification is accomplished by a titanium getter furnace operating at about 800°C. The temperature is measured by a chromel-alumel thermocouple connected to a Sim-Ply-Trol pyrometer. The furnace consists simply of an Inconel tube approximately 26 inches long and 2-1/2 inches in diameter. The tube is filled with titanium sponge and the central portion of the tube is heated by a Marshal tube furnace.

Final purification is achieved by passing the gas through a Mine Safety Appliances Corp. Model 15 NaK bubbler. The NaK bubbler is stock except for the drainage valves which were replaced by Hoke HY 473 stainless bellows valves welded in place. Upon entering the bubbler, the gas first passes through a "hot leg" containing about 1/3 pound of NaK (44-56% K) at 300°C; the temperature being measured by an iron-constantan thermocouple connected to a Sim-Ply-Trol pyrometer. It then passes through a "cold-leg" containing the same amount of NaK at room temperature, and then through a demister to remove any entrained alkali metal vapor. A glass catch-trap is attached to the bubbler exit for visual observation purposes.

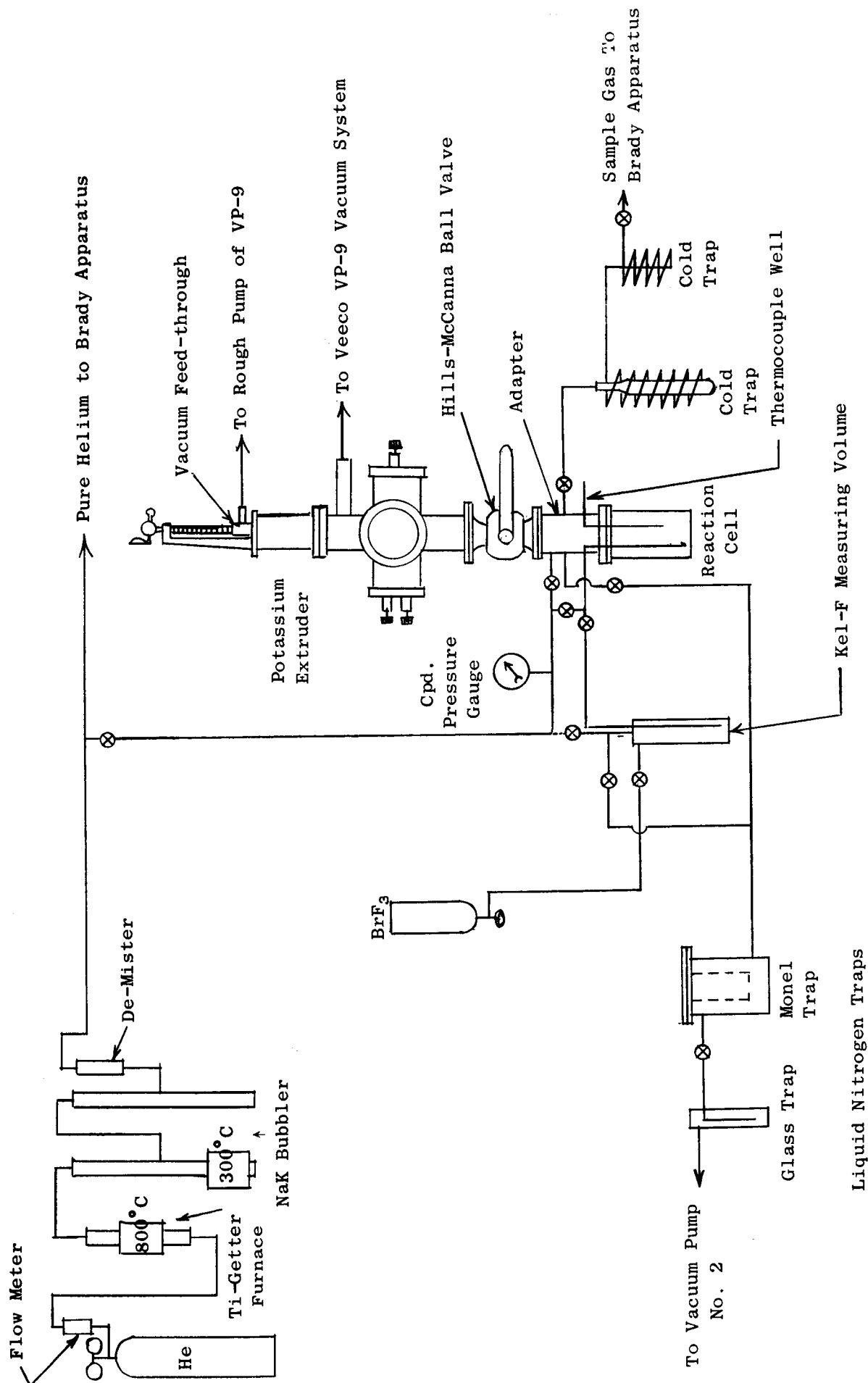


FIGURE 1 System for BrF₃ Determination of Oxygen in Alkali Metals

Purified helium leaving the purification system normally contains only about 0.2 ppm of oxygen as measured by the Brady apparatus. The entire purification system is shown in Figure 2.

B. The Analytical System

The analytical system is illustrated in Figure 3. The various components are mounted on a Flexangle frame and enclosed in a hood. Purified helium, carried into the hood via 1/4" copper tubing, is supplied to the various components requiring it by a manifold, also constructed of 1/4" copper tubing, and assembled by means of solder tube connections.

The Matheson bromine trifluoride cylinder, mounted in an inverted position, can be seen in the upper left hand corner of Figure 3. The BrF_3 is fed directly from the cylinder into the Kel-F measuring volume shown in Figure 4, which is an exact copy of the one used at Argonne National Laboratories. Detailed plans for its construction are illustrated in Drawings 4012286-191 and -192 and the Kel-F tube itself is shown in Drawing 4012286-193. The liquid bromine trifluoride is transferred to the tube by first evacuating the tube and then opening the cylinder valves. It is then transferred to the evacuated reaction cell by pressurizing the tube with helium. An earlier model of the apparatus had a separate storage cell where the BrF_3 could be purified by exposure to vacuum and bubbling with helium. This was later found to be unnecessary; adequate purification being readily achieved in the reaction cell itself. When fresh BrF_3 is added to the already pre-fluorinated cell, no increase in the helium blank rate is observed provided the usual pump-out procedure prior to analysis is observed. Apparently, all of the gaseous impurities present in the BrF_3 have either a sufficiently high vapor pressure to be removed by pumping or a freezing point high enough to prevent their passage through the effluent cold traps ($\sim -130^\circ\text{C}$). to the Brady apparatus.

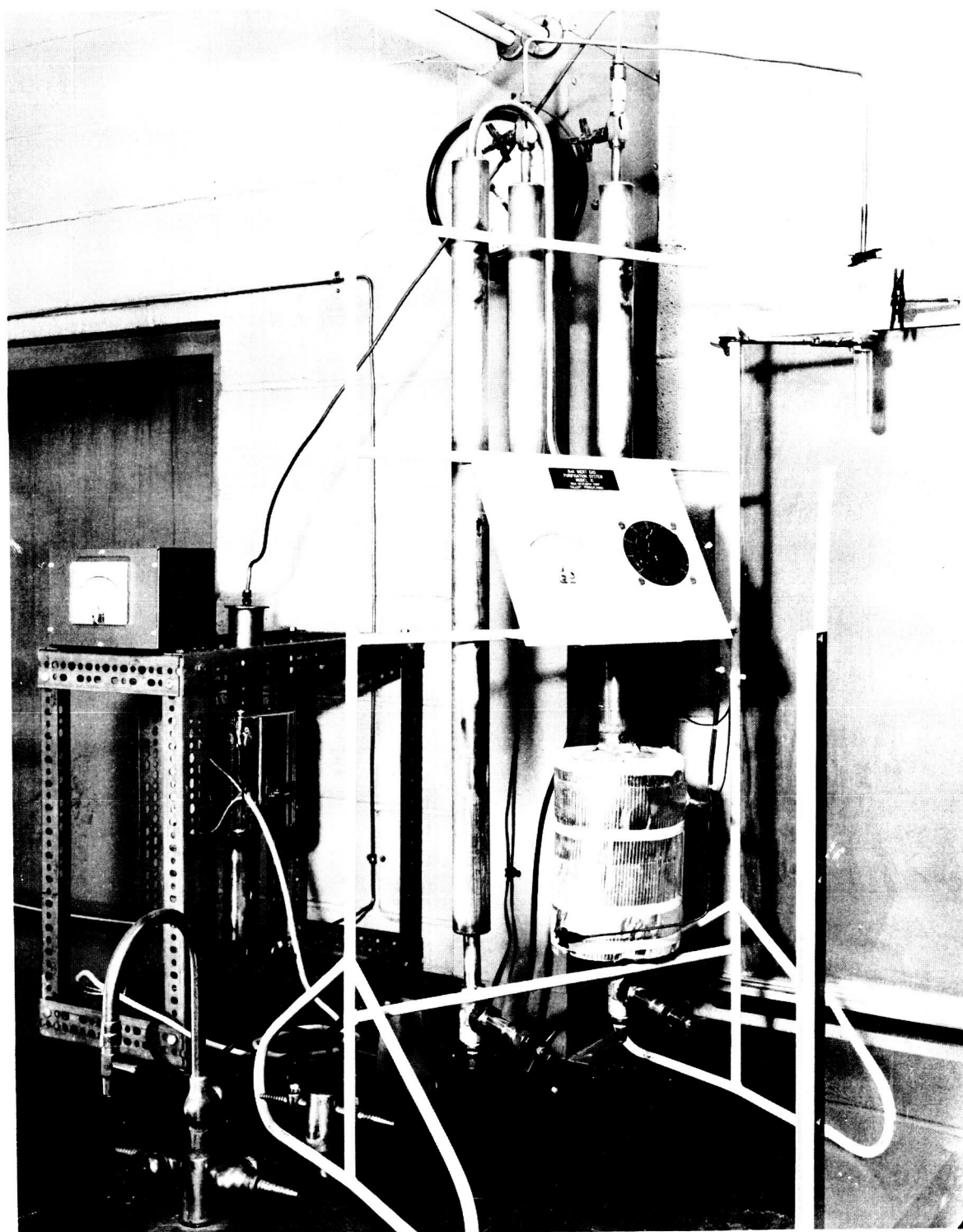


FIGURE 2 Helium Purification System - Titanium Sponge Furnace and NaK Bubbler

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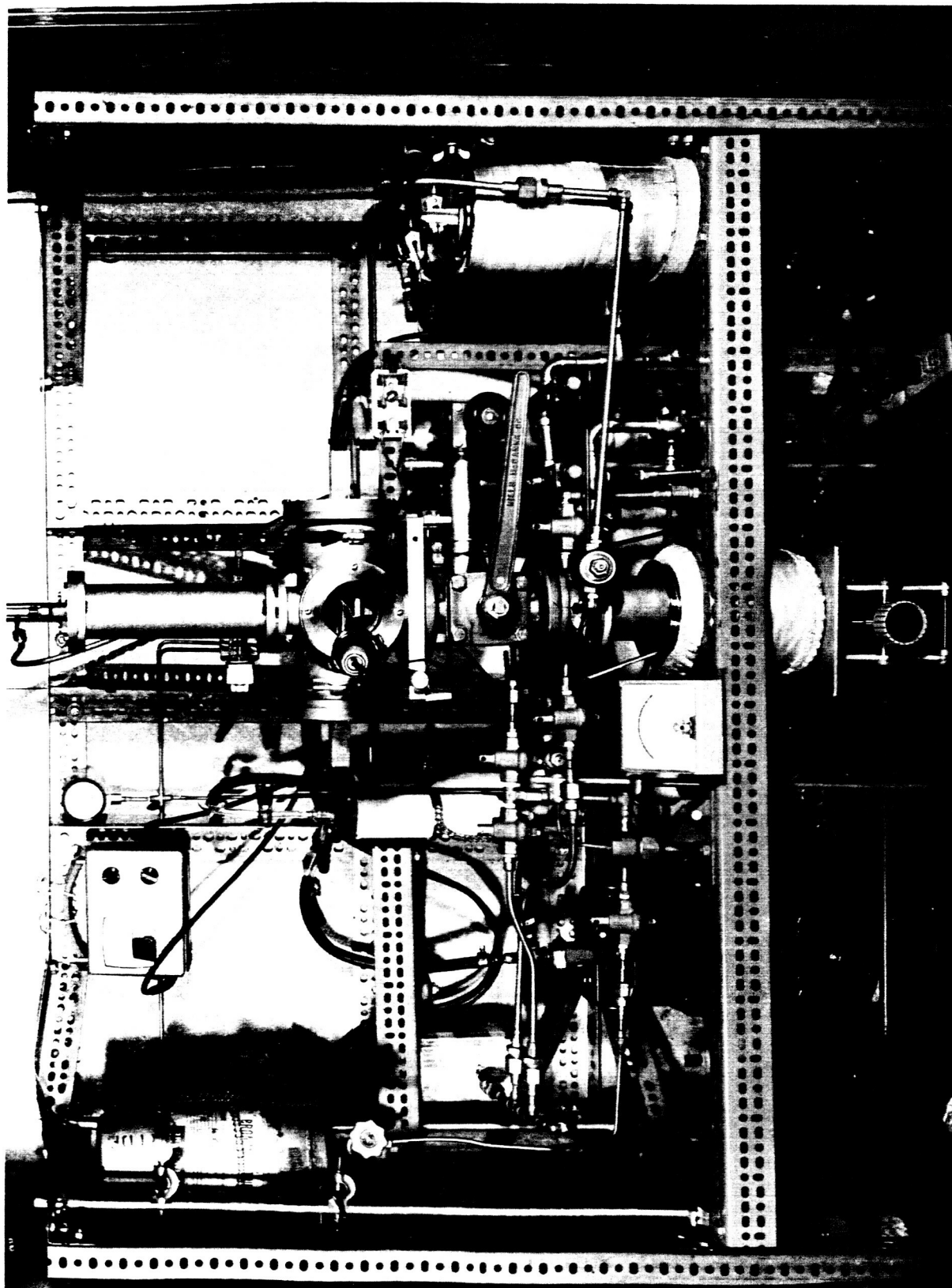


FIGURE 3 Analytical System for the Determination of Oxygen in Potassium Metal

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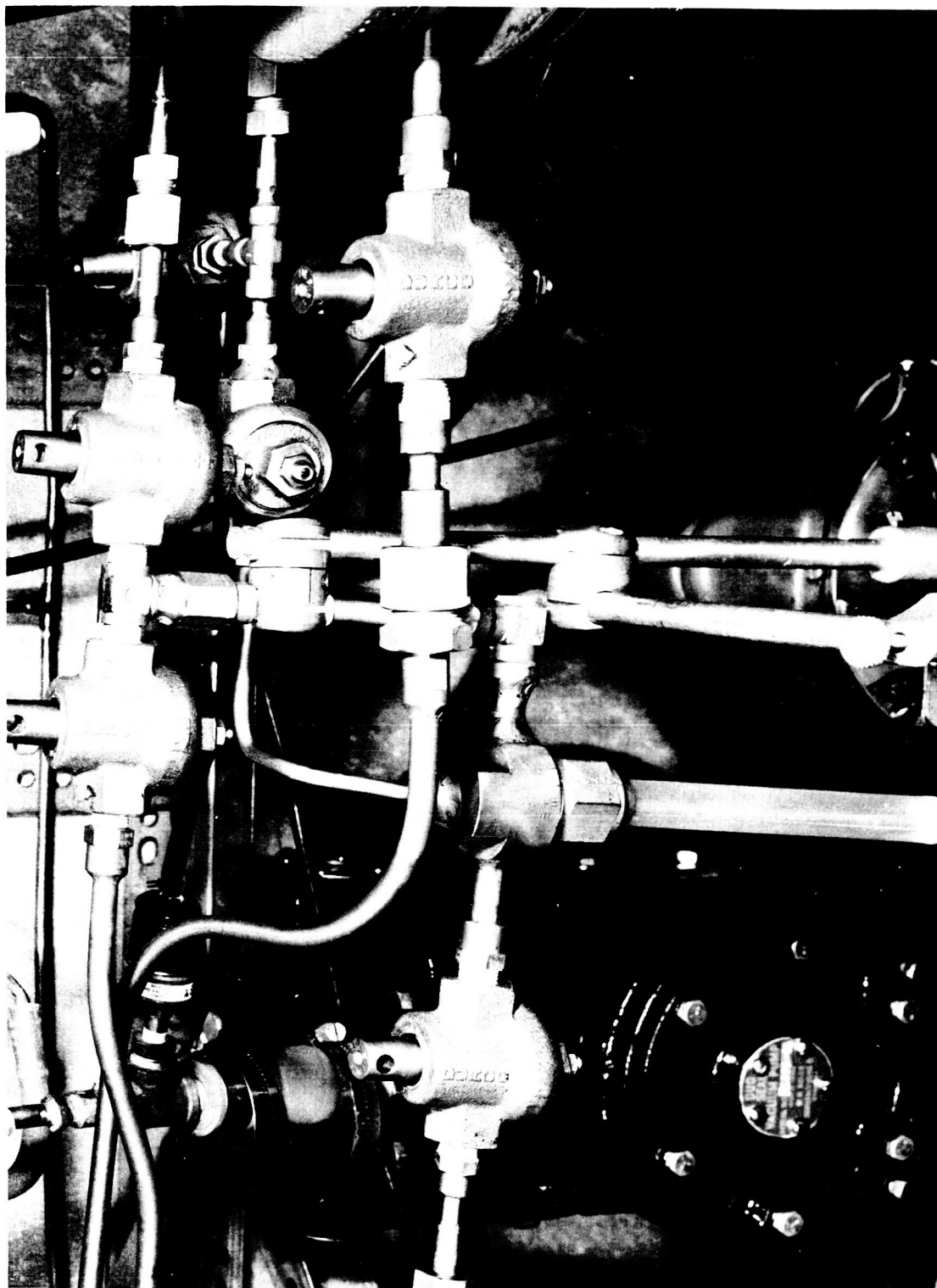
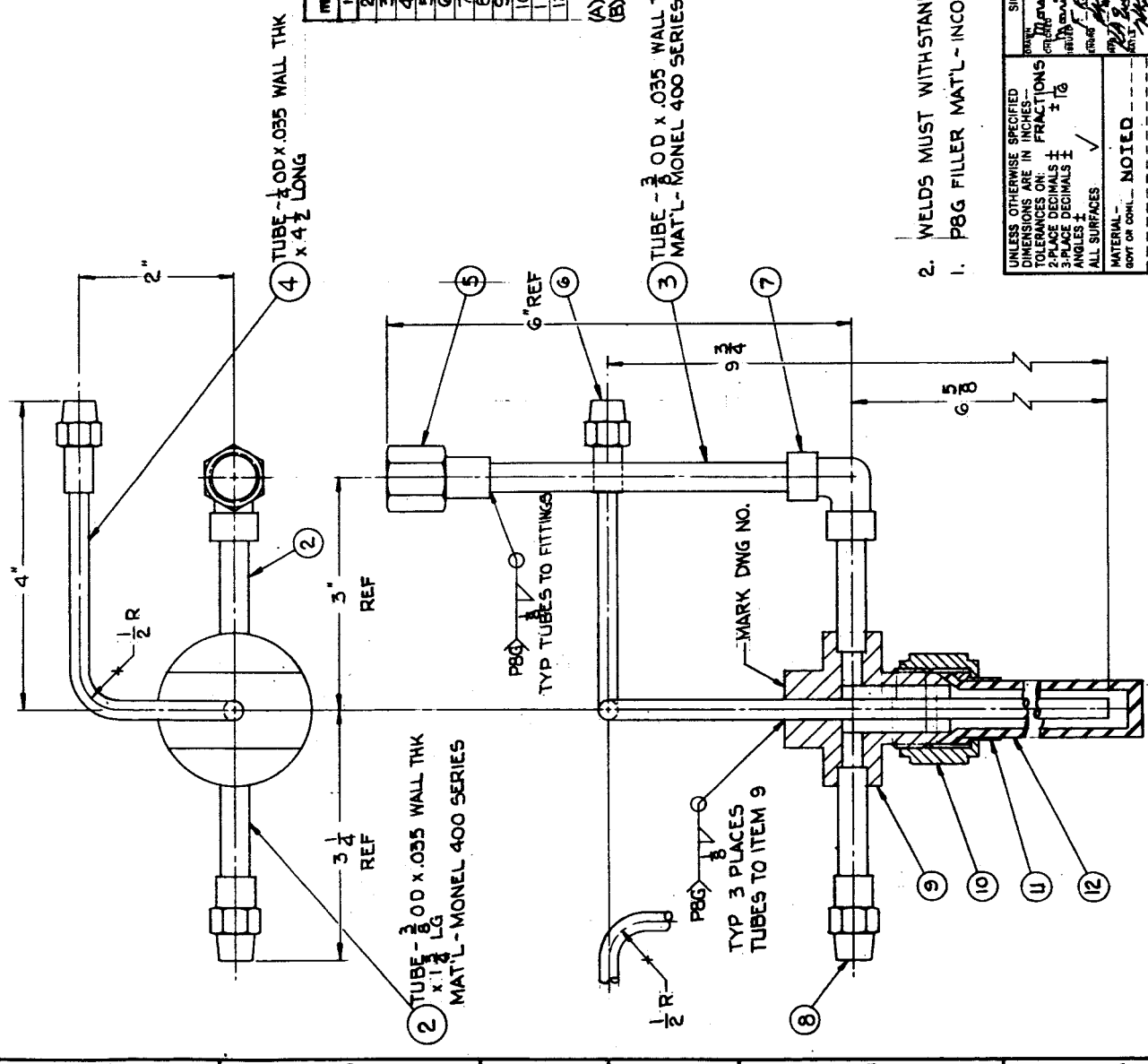


FIGURE 4 Kel-F Measuring Volume

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REV	4012286-191
DATE	APPROVED
REVISIONS	
SYM	ZONE



ITEM	IDENTIFICATION NO.	DESCRIPTION OR NAME	ZONE	GROUP NO. & QTY
1		NUT	AG	1
2	4012286-191 P2	TUBE	D7	2
3	P3	TUBE	C4	1
4	P4	TUBE	D4	1
5	MGSW-7-6	FEMALE CONNECTOR	(A) D4	1
6	MGSW-1-4	MALE CONNECTOR	(A) C4	1
7	MGSW-9	ELBOW	(A) B4	1
8	MGSW-1-6	MALE CONNECTOR	(A) B7	1
9	4012286-192 P1	FITTING FOR KEL-F TRAP	B7	1
10	12 BTX-55	NUT	(B) B7	1
11	12 TX-5	SLEEVE	(B) A7	1
12	4012286-193 P1	KEL-F TUBE	A7	1

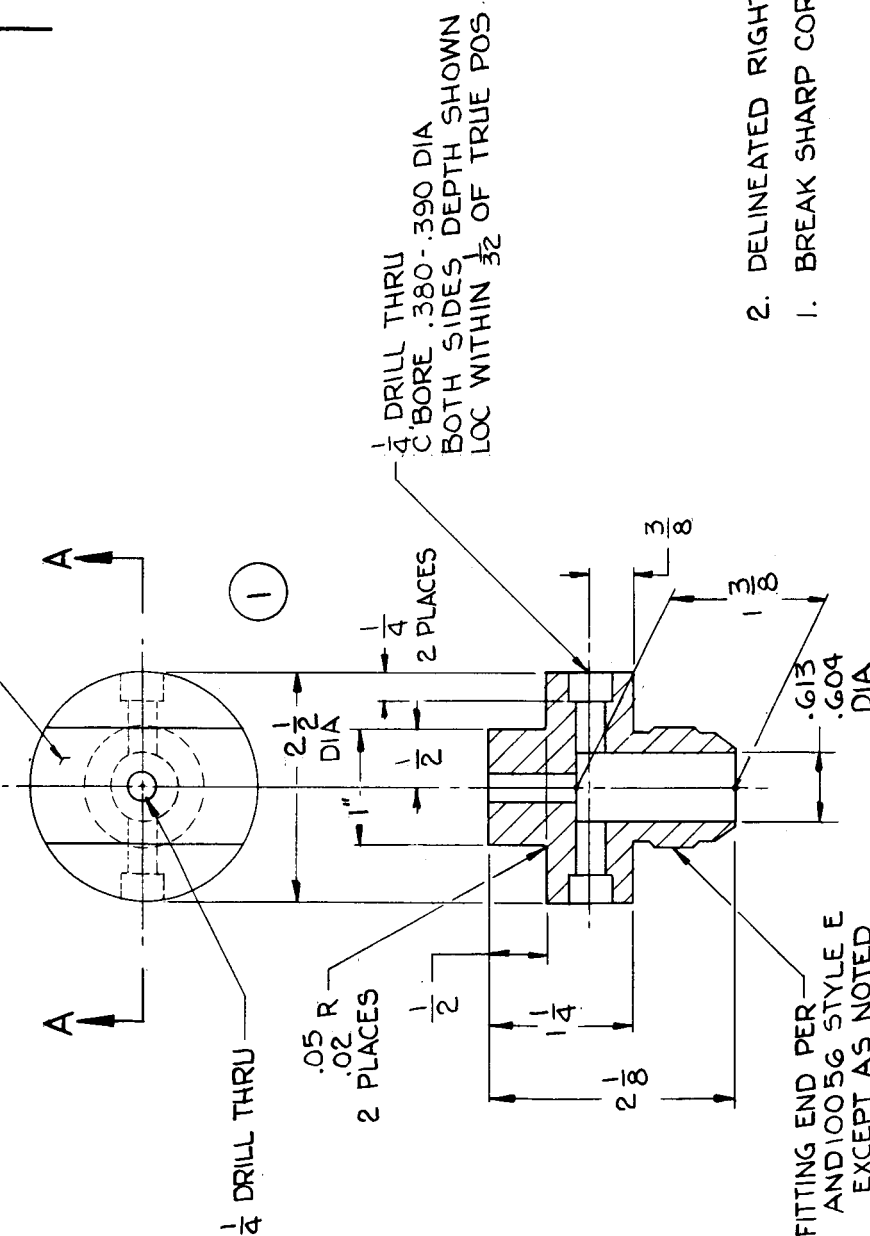
(A) CAJON COMPANY - CLEVELAND, OHIO
(B) PARKER APPLIANCE COMPANY - CLEVELAND, OHIO

- WELDS MUST WITHSTAND $10^{-5} - 10^{-6}$ TORR WITH NO LEAKS
- P8G FILLER MAT'L - INCO 60

GENERAL ELECTRIC		AFJD - DEPT LOG-ENVENDALE PLANT	
DATE 4/20/64		TITLE KEL-F TRAP FOR BROMINE TRIFLUORIDE	
SIGNATURES		CONTRACT NO. 4012286-191	
UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES-- TOLERANCES ON: 2 PLACE DECIMALS $\pm .10$ 3 PLACE DECIMALS $\pm .01$ ANGLES $\pm 1^\circ$ ALL SURFACES		CODE IDENT NO. C	
MATERIAL - NOTED		SCALE 1/1	
DOVT OR CONL		SHEET 1 OF 1	
DR		PL-189	

SIZE	B	4012286-192	SHEET	REV
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SYM	DESCRIPTION			

MARK DWG NO.



SECT A-A

1. BREAK SHARP CORNERS .015 MAX RAD OR CHAM
2. DELINEATED RIGHT ANGLES ARE $90^\circ \pm 15'$

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± 1/9353610491084751924707685					

The reaction cell itself is constructed of 3" Monel pipe heliarc-welded to a 3/8" flange fitted with a Teflon "O"-ring. The cell is mated to a 2" Hills-McCanna monel ball valve via an adapter which provides the necessary vacuum, helium, and bromine trifluoride connections. The relationship of these parts may be seen clearly in Figure 5. Details of construction may be seen in Drawings 4012093-785 and -787. The function of the adapter and the various connections thereto can be better observed in Drawing 4012286-182. The 1/4" dip-leg through which BrF_3 is introduced serves also as a helium inlet so that the gas may be bubbled through the liquid BrF_3 during the course of an analysis. The other helium inlet permits the cell to be purged while the BrF_3 is frozen. A thermocouple well containing a copper-constantan thermocouple is provided for temperature measurement; the temperature being read by means of an Assembly Products, Inc., direct reading pyrometer calibrated from -220°C to $+40^\circ\text{C}$.

The sample gas is removed from the reaction cell by purging with helium, which then carries the gas to the Brady apparatus for measurement of the oxygen. En route, the gas must pass through two effluent cold traps at -130°C in order to remove any BrF_3 or any reaction products which might otherwise interfere with the analysis. These traps are constructed quite simply of 3/8" monel tubing and are illustrated in Figure 6. The first trap has a large entry tube of 1" OD monel in order to prevent plugging and both traps are surrounded by Dewar flasks containing pentane slush. With these traps, helium blank rates of 5-6 micrograms of oxygen per hour can be maintained with the reaction cell at room temperature. As will be shown later, the blank rate is dependent upon reaction cell temperature.

The various components of the analytical system may be evacuated via a manifold constructed of 3/8" monel tubing leading to a Welch 1405 mechanical pump. In order to protect the pump from corrosive vapors, two liquid nitrogen cold traps are used. The first is a large capacity monel trap illustrated in Figure 7. Details of its construction are shown in Drawings 4012093-786 and 4012286-171. Following this trap is another of glass which removes any final traces of BrF_3 or other corrosive vapors.

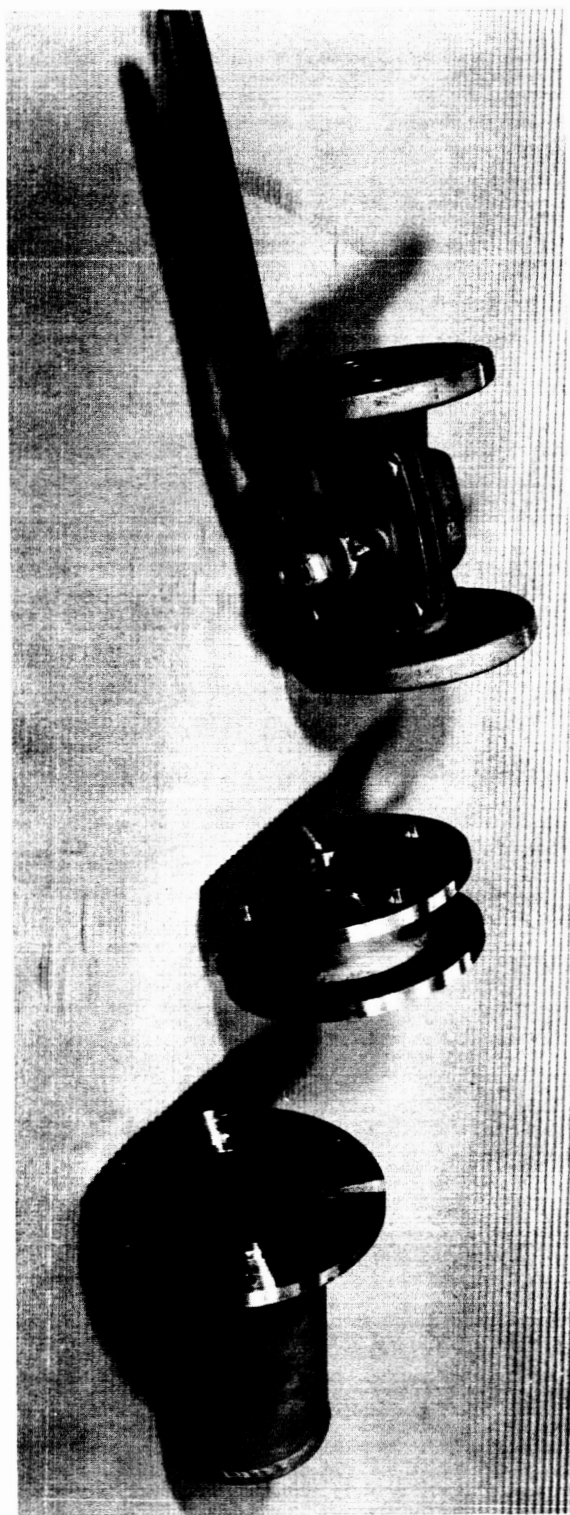
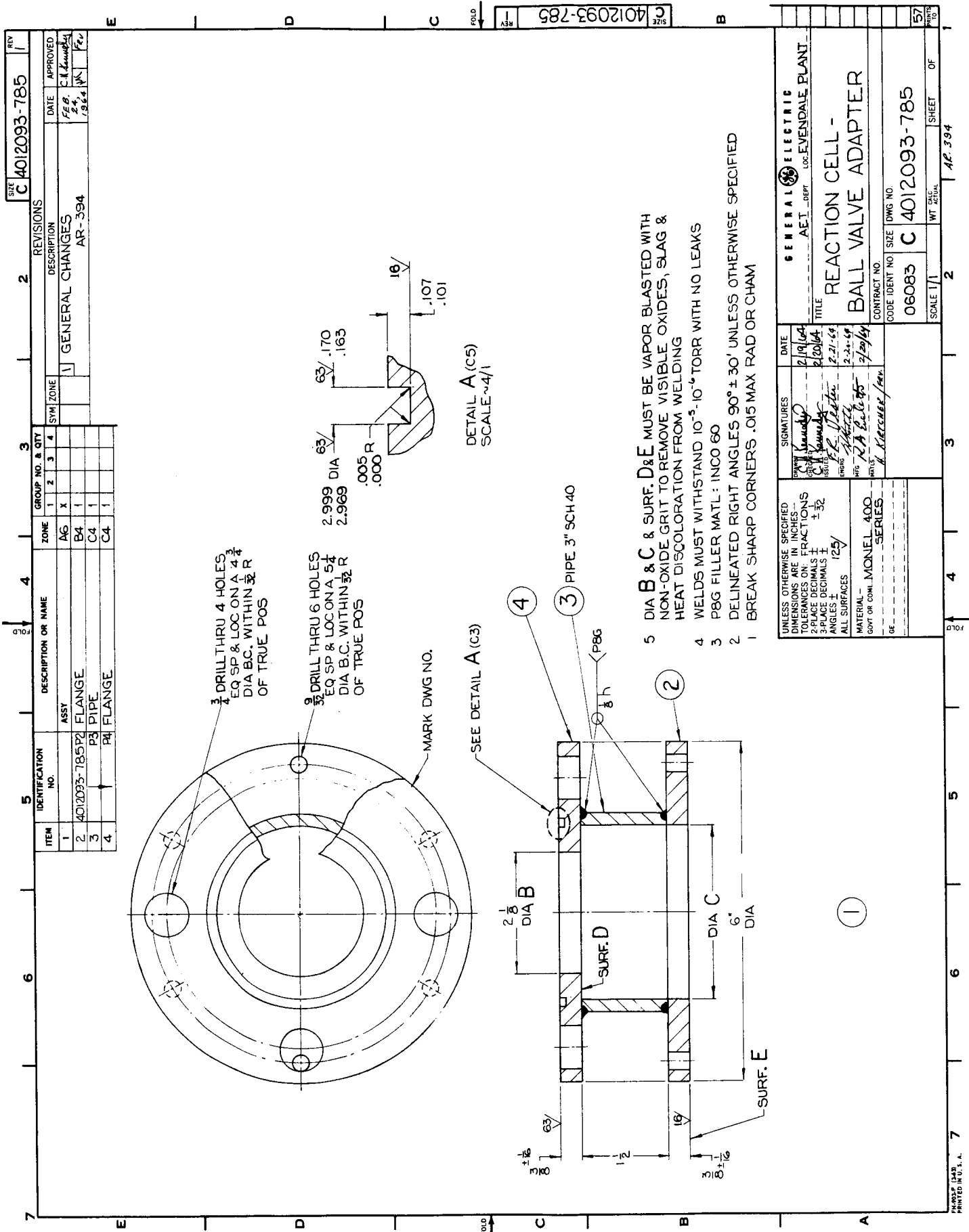


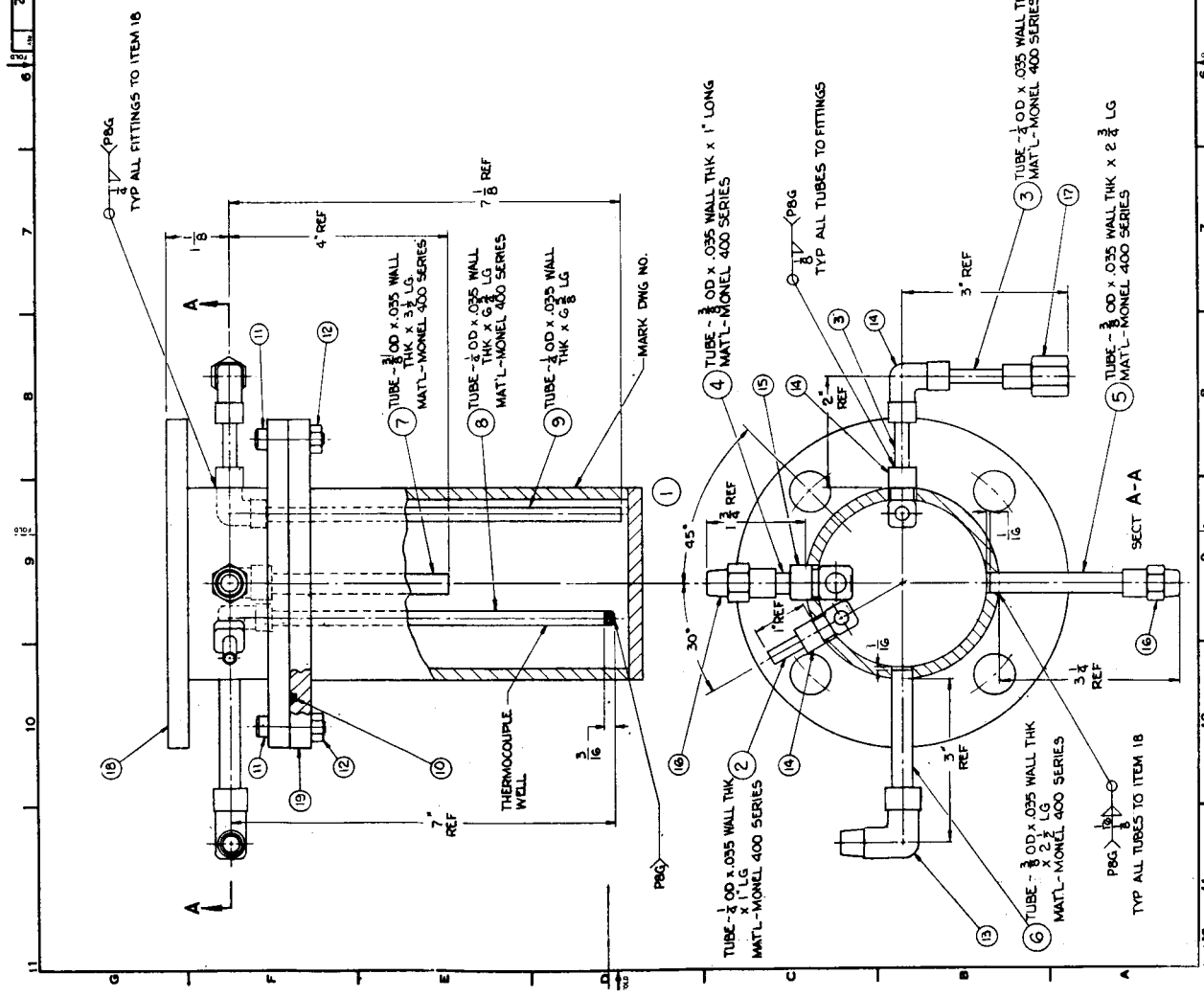
FIGURE 5 Monel Ball Valve-Adapter-Reaction Cell Combination

C 64040819



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2	4012286-182	TUBE	1	1	1	1		
3	4012286-182	TUBE	1	1	1	1		
4	4012286-182	TUBE	1	1	1	1		
5	4012286-182	TUBE	1	1	1	1		
6	4012286-182	TUBE	1	1	1	1		
7	4012286-182	TUBE	1	1	1	1		
8	4012286-182	TUBE	1	1	1	1		
9	4012286-182	TUBE	1	1	1	1		
10	4012286-182	TUBE	1	1	1	1		
11	4012286-182	TUBE	1	1	1	1		
12	4012286-182	TUBE	1	1	1	1		
13	4012286-182	TUBE	1	1	1	1		
14	4012286-182	TUBE	1	1	1	1		
15	4012286-182	TUBE	1	1	1	1		
16	4012286-182	TUBE	1	1	1	1		
17	4012286-182	TUBE	1	1	1	1		
18	4012286-182	TUBE	1	1	1	1		
19	4012286-182	TUBE	1	1	1	1		

(A) CAJON COMPANY - CLEVELAND, OHIO



1. PBG FILLER MAT'L - INCO 60
2. WELDS MUST WITHSTAND 10^{-5} TO 10^{-6} TORR WITH NO LEAKS

DATE	4/10/60	DESIGNED BY	J. J. J.
DATE	4/10/60	CHECKED BY	J. J. J.
DATE	4/10/60	APPROVED BY	J. J. J.
DATE	4/10/60	CONTRACT NO.	4012286-182
DATE	4/10/60	SCALE	1/1
DATE	4/10/60	SHEET	1 OF 1
DATE	4/10/60	PL	189

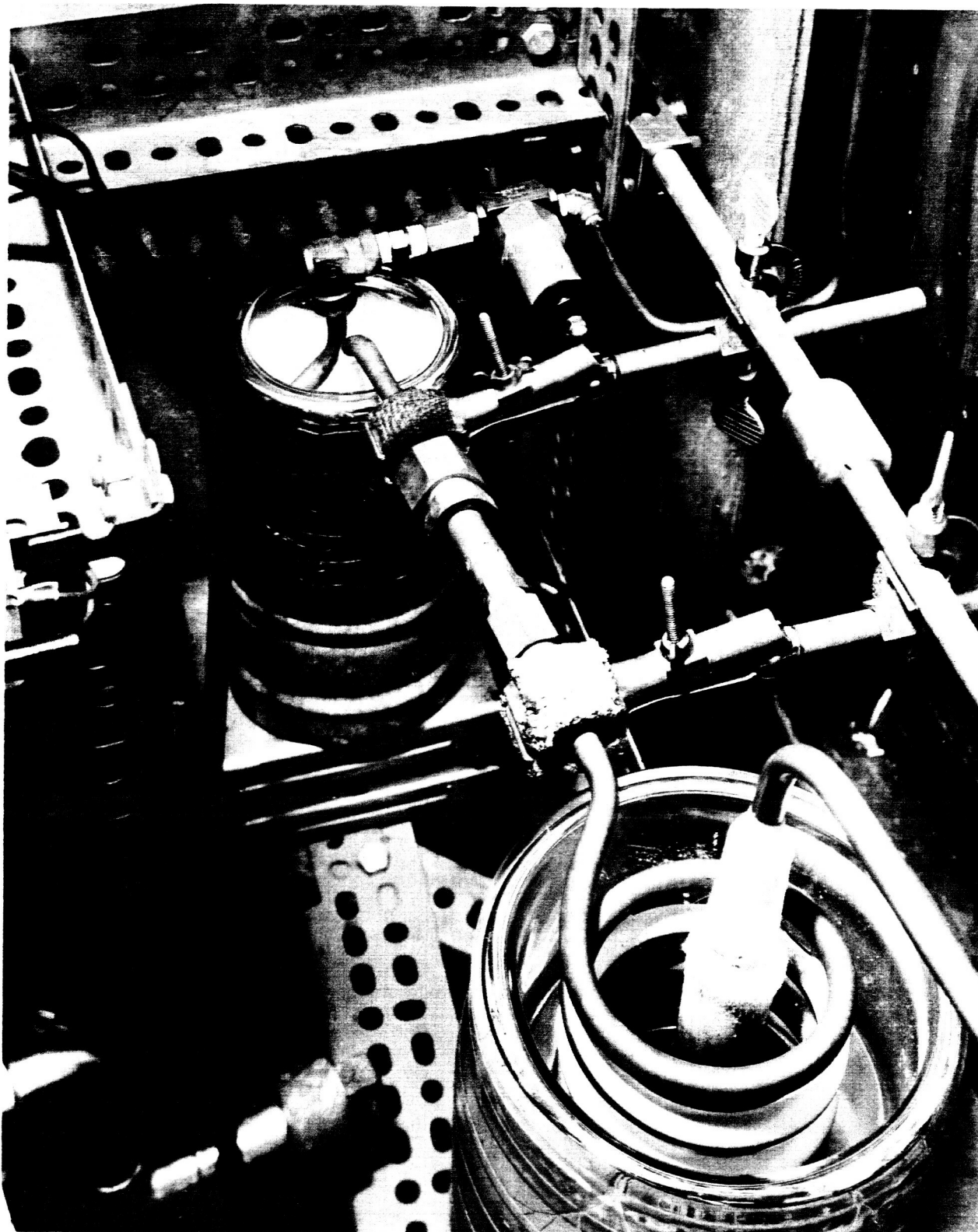


FIGURE 6 Effluent Cold Traps

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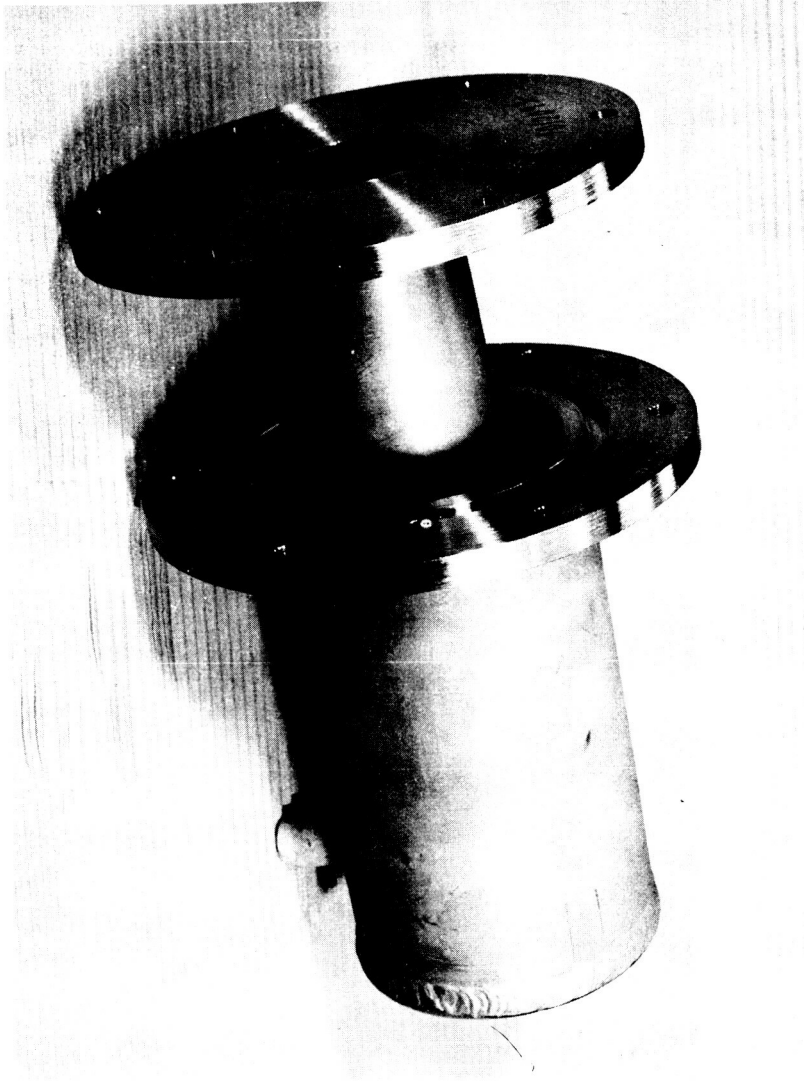
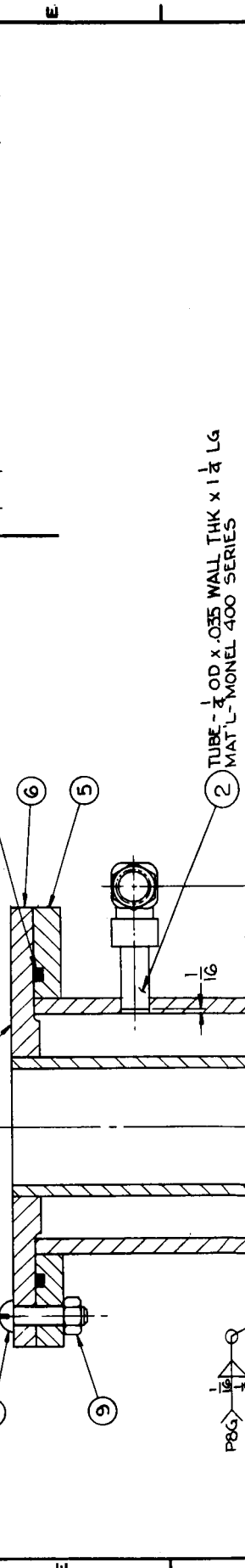


FIGURE 7 Monel Cold Trap Assembly

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REV	DATE	DESCRIPTION	APPROVED
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2			
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ITEM	IDENTIFICATION NO.	DESCRIPTION OR NAME	ZONE	GROUP NO. & QTY			
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1		WAST	A5	1			
2	4012286-171P2	TUBE	D4	1			
3	↓ P3	TUBE	C5	1			
4	↓ P4	TUBE	C7	1			
5	4012093-787 G1	TRAP	E4	1			
6	4012093-786 G1	INNER TRAP MEMBER	E4	1			
7	M529513-242	O-RING	E4	1			
8	COM'L STN STL	RD HD CAP SCR 1/4 UNC x 1 1/4 LG	E7	6			
9	COM'L STN STL	HEX NUT 1/4 UNC	E7	6			
10	M6VC	VACUUM COUPLING	(A) C7	1			
11	M45W-9	ELBOW	(A) C5	1			
12	M65W-1-G	MALE CONNECTOR	(A) C5	1			

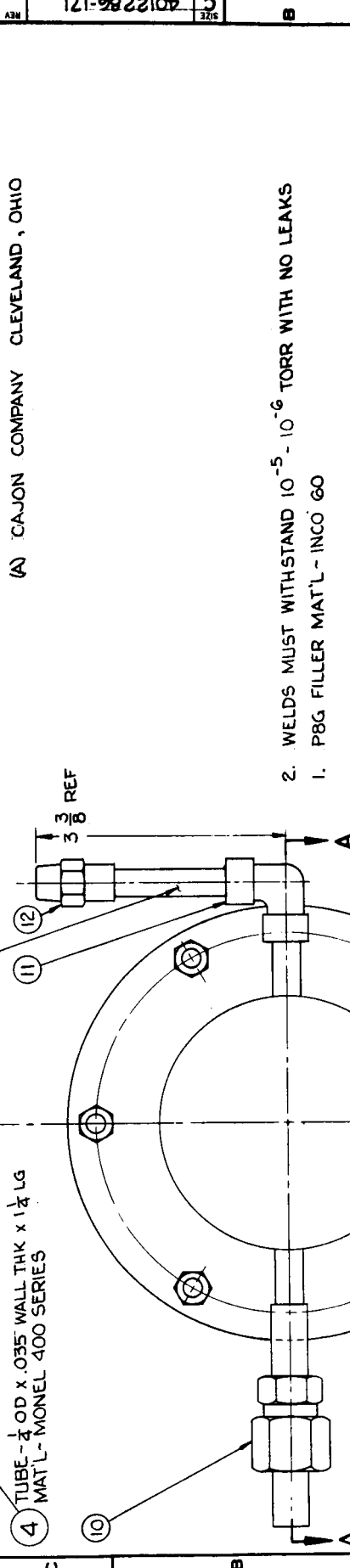
8" 1 1/2" REF

8" 1 1/2" REF

1/16"

3/8" OD x 0.035 WALL THK x 2 1/2" LG

(A) CAJON COMPANY CLEVELAND, OHIO



UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES - TOLERANCES ON FRACTIONS 2 PLACE DECIMALS ± 1/16 3 PLACE DECIMALS ± 1/32 ALL SURFACES ✓		DATE 6/20/64	
SIGNATURES DESIGNED BY: J. J. Gorman CHECKED BY: J. J. Gorman APPROVED BY: F. R. Heister		TITLE ROUGH TRAP	
MATERIAL - SOFT OR COM'L NOTED		CONTRACT NO. 4012286-171	
CODE IDENT NO. SIZE DWG NO. C		SHEET 1 OF 1	

Interconnecting lines between the reaction cell, measuring volume, cold traps, and rough vacuum system are of 1/4" or 3/8" Monel tubing--the larger size predominating. Connections are made by means of socket-weld Monel fittings, threaded connectors, or Cajon ultra-high vacuum monel connectors with Teflon gaskets--the last generally being used at points where frequent disassembly was expected. All threaded connections were sealed with Teflon tape. Monel 1/4" Durco plug valves were used extensively. An exploded view of this valve is shown in Figure 8. Hoke 482 bellows valves were used in helium lines where exposure to BrF_3 was not a problem, and one Hoke M 440 was used to separate the analytical system from the Brady apparatus.

The potassium extruder is essentially the same as that used by NASA and is shown in Figure 3 and close up in Figure 9. A complete set of engineering drawings and specifications are shown in Drawings 4012286-444 through -450. Modifications such as bellows sealed activator rods and a vacuum feed-through for the extrusion rod are illustrated in Figures 10 and 11. Connection to the high vacuum system is accomplished by means of extension with a 3.5" flange at the rear of the extruder. This extension (shown in Drawing 4012286-445) also connects to a Veeco RG-75 ion gauge with which pressures as low as 5×10^{-7} mm Hg have been measured. The high vacuum for the extruder is supplied by means of a Veeco VP-9 pumping system using a water-cooled diffusion pump and a Welch 1402 fore pump. The pumping capacity of the system is rated at about 85 liters per second with a backstreaming rate of about .003 cc per hour at 25°C.

C. The Oxygen Measuring System

Oxygen measurement is accomplished by a modified Brady apparatus^(6,7) in which oxygen, carried in the helium stream, reacts quantitatively with an alkaline solution of sodium anthraquinone- β -sulfonate. The previously reduced solution is thereby decolorized; the change in absorbance being a measure of the amount of oxygen present.

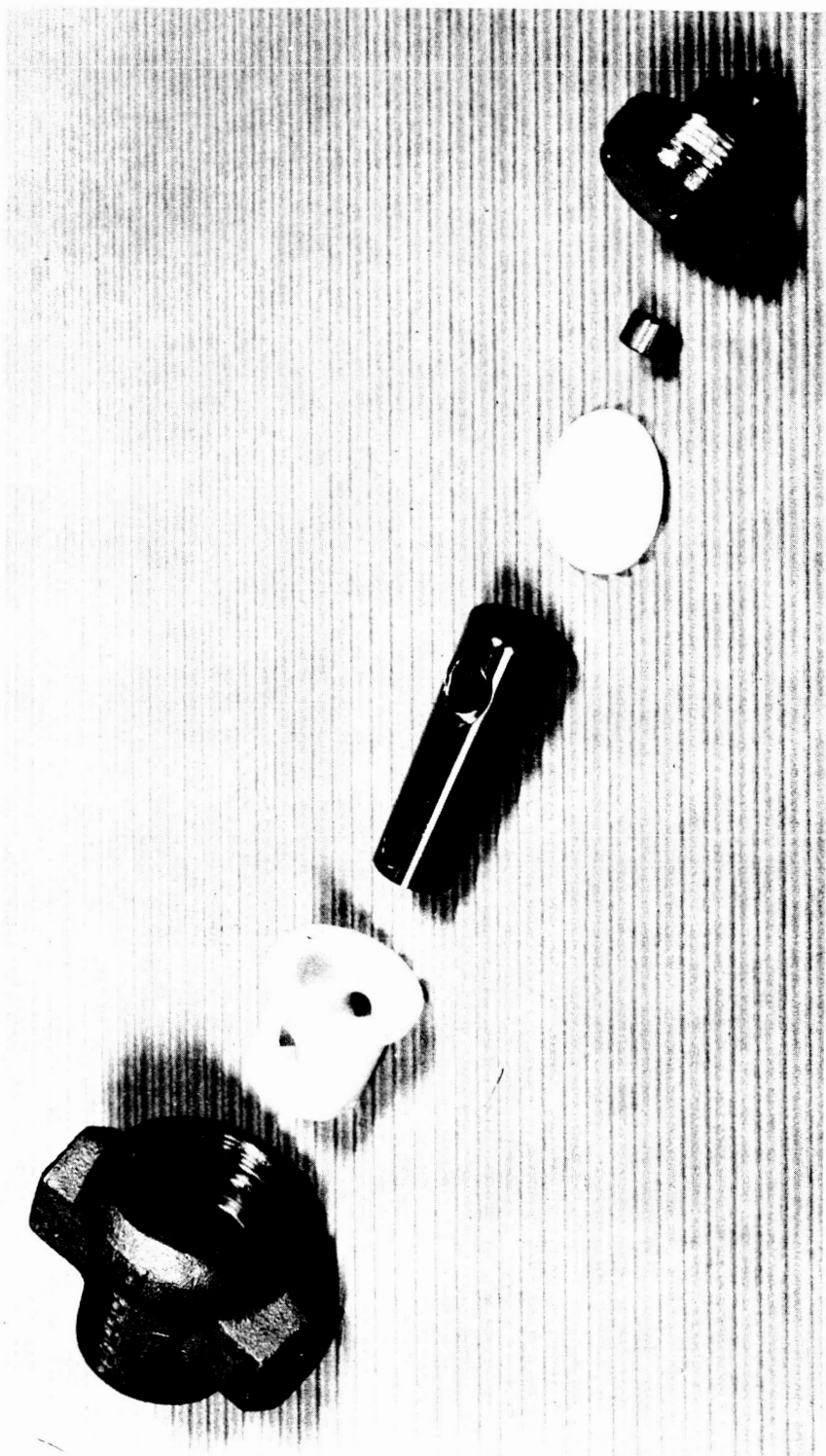


FIGURE 8 Expanded View of All Monel-Teflon Durco Plug Valve

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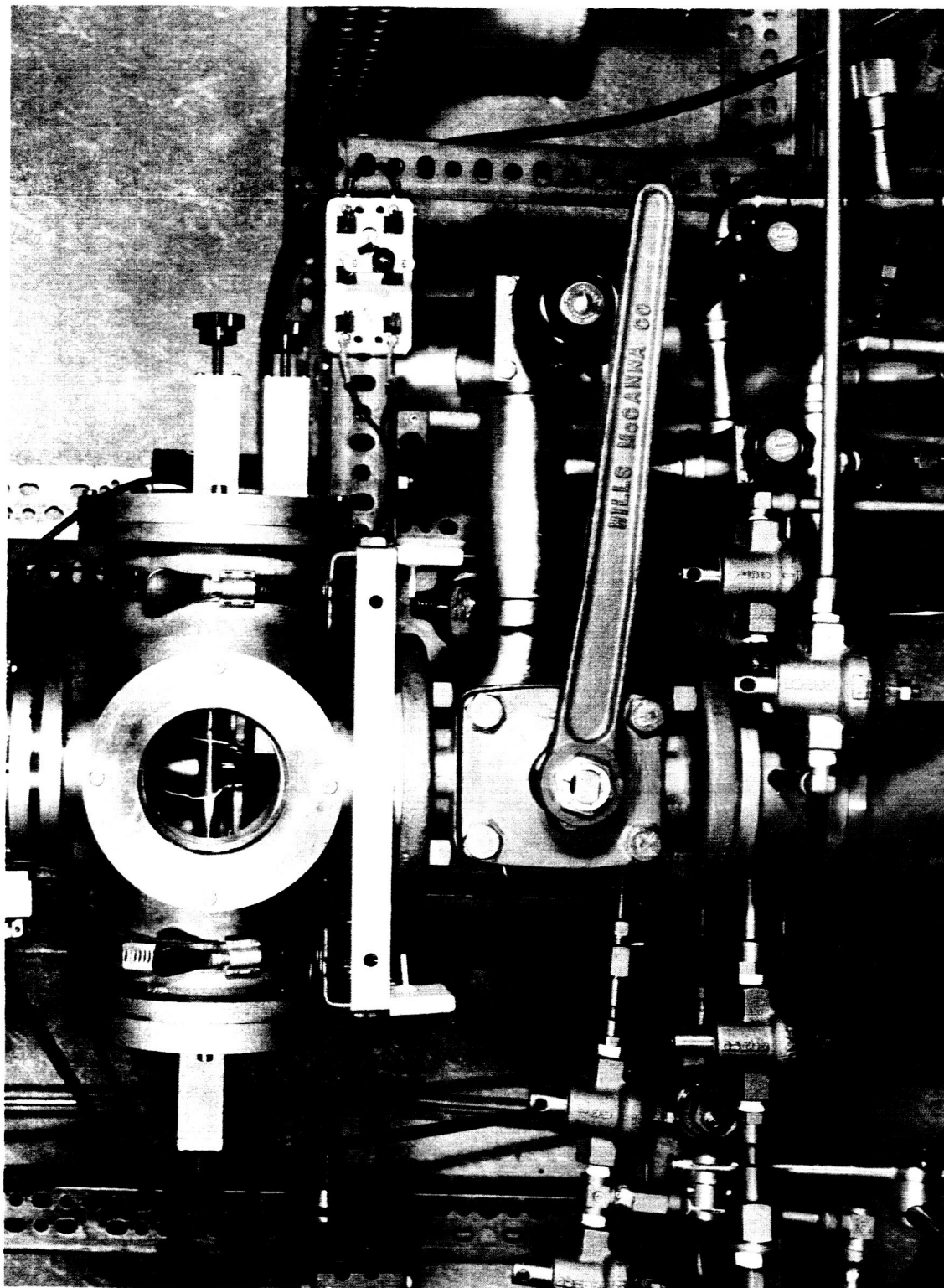
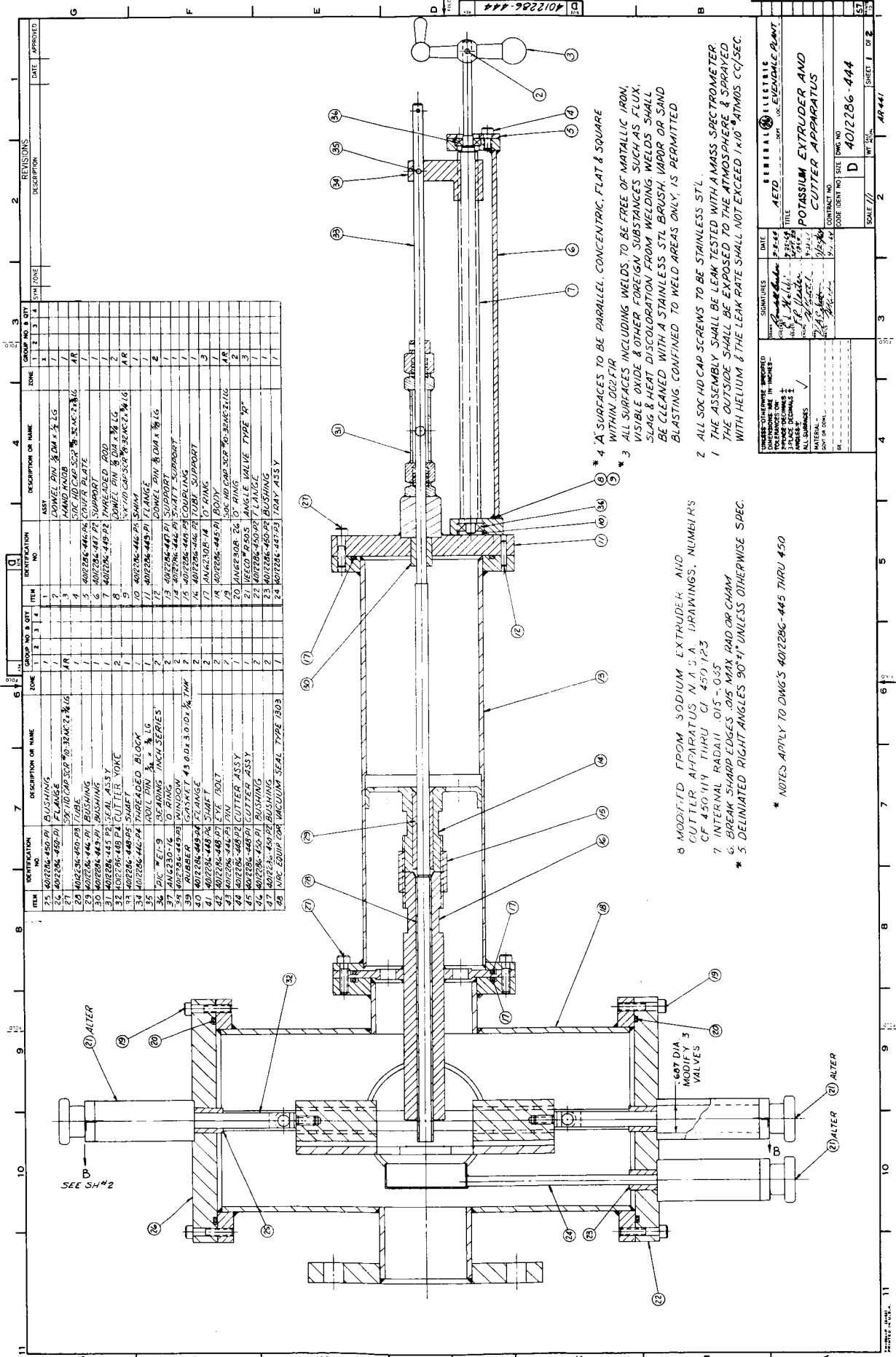
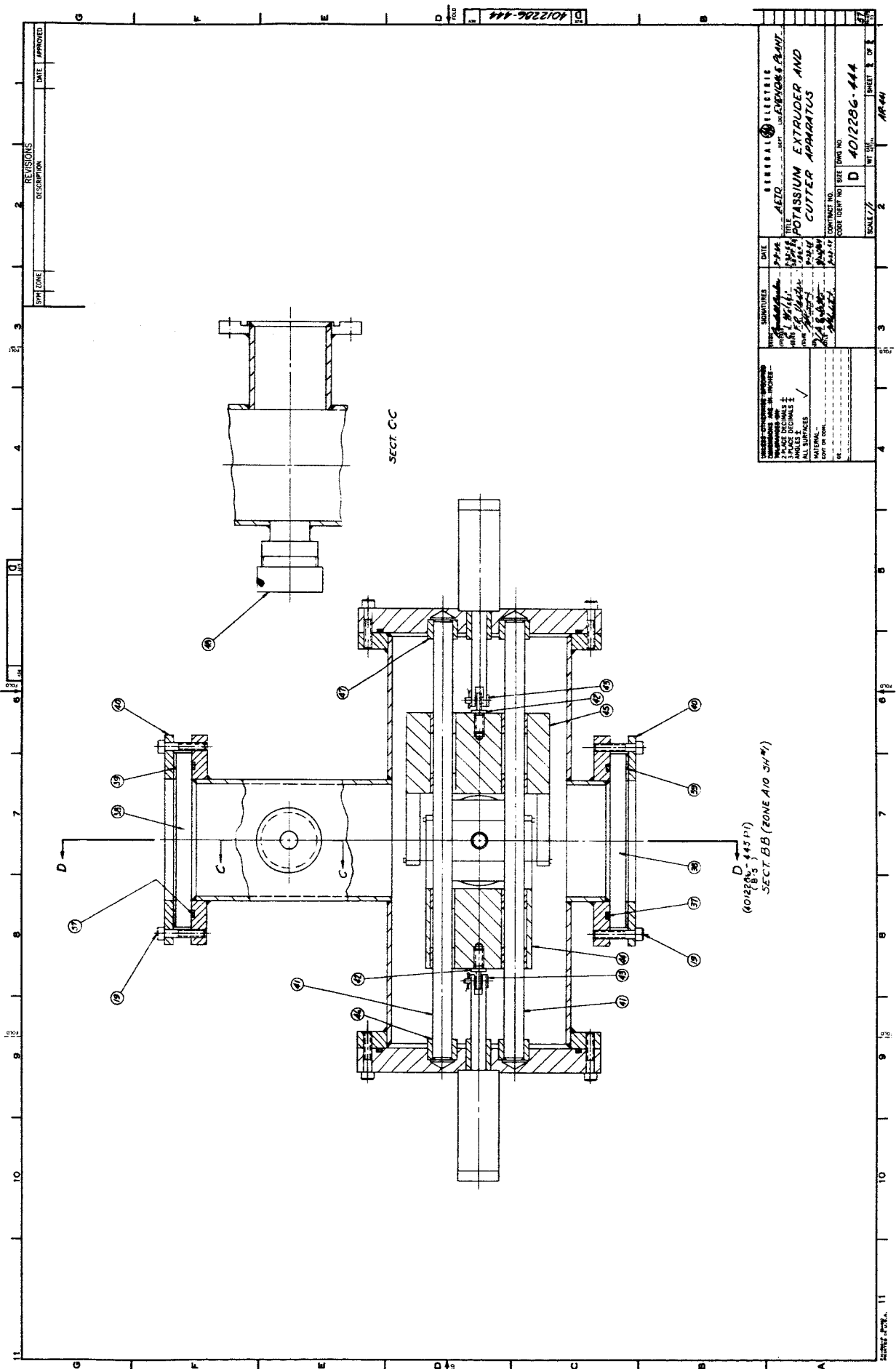


FIGURE 9 Potassium Extruder, Ball Valve and Reaction Cell Assembly

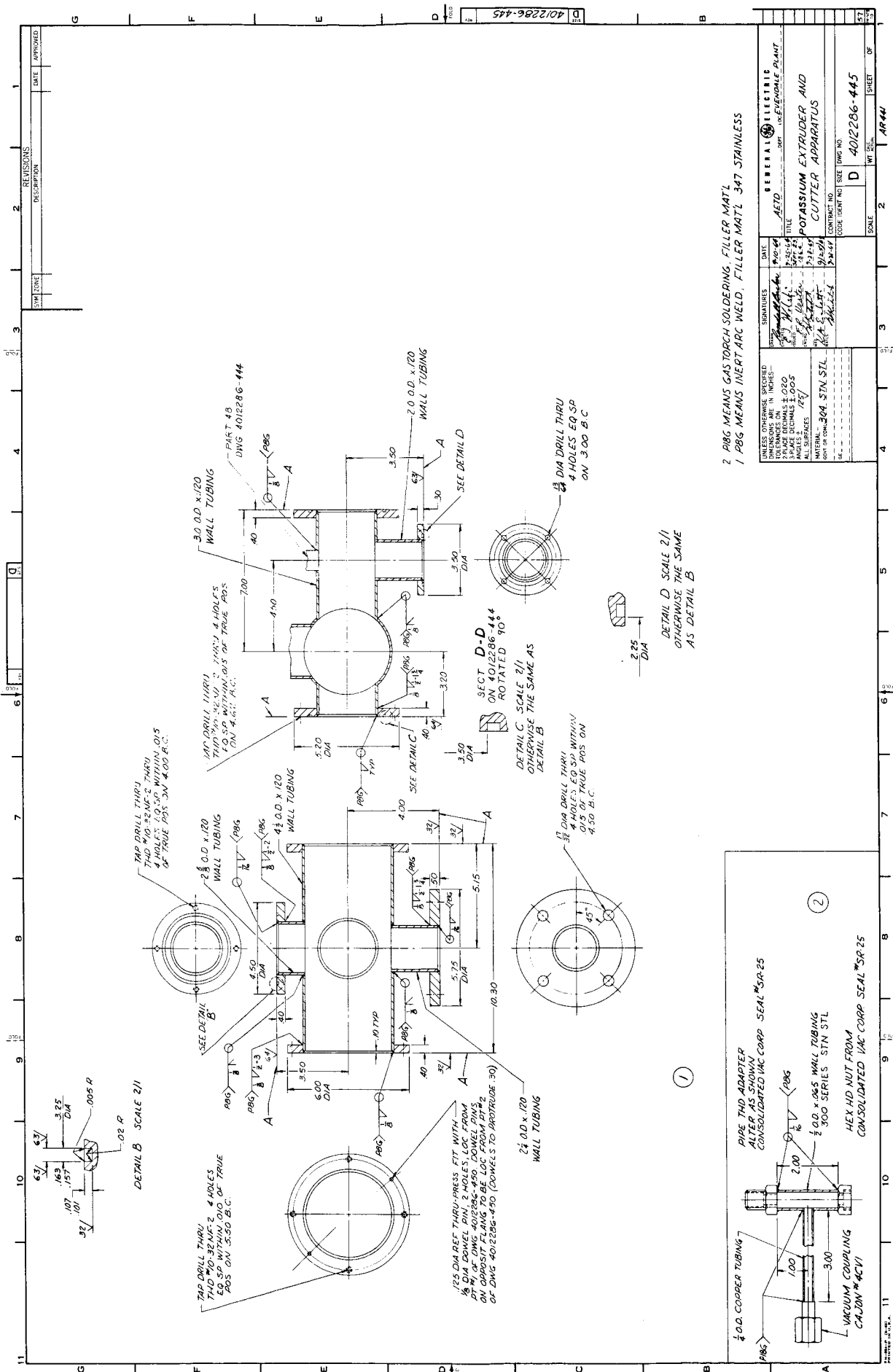
C 64062552

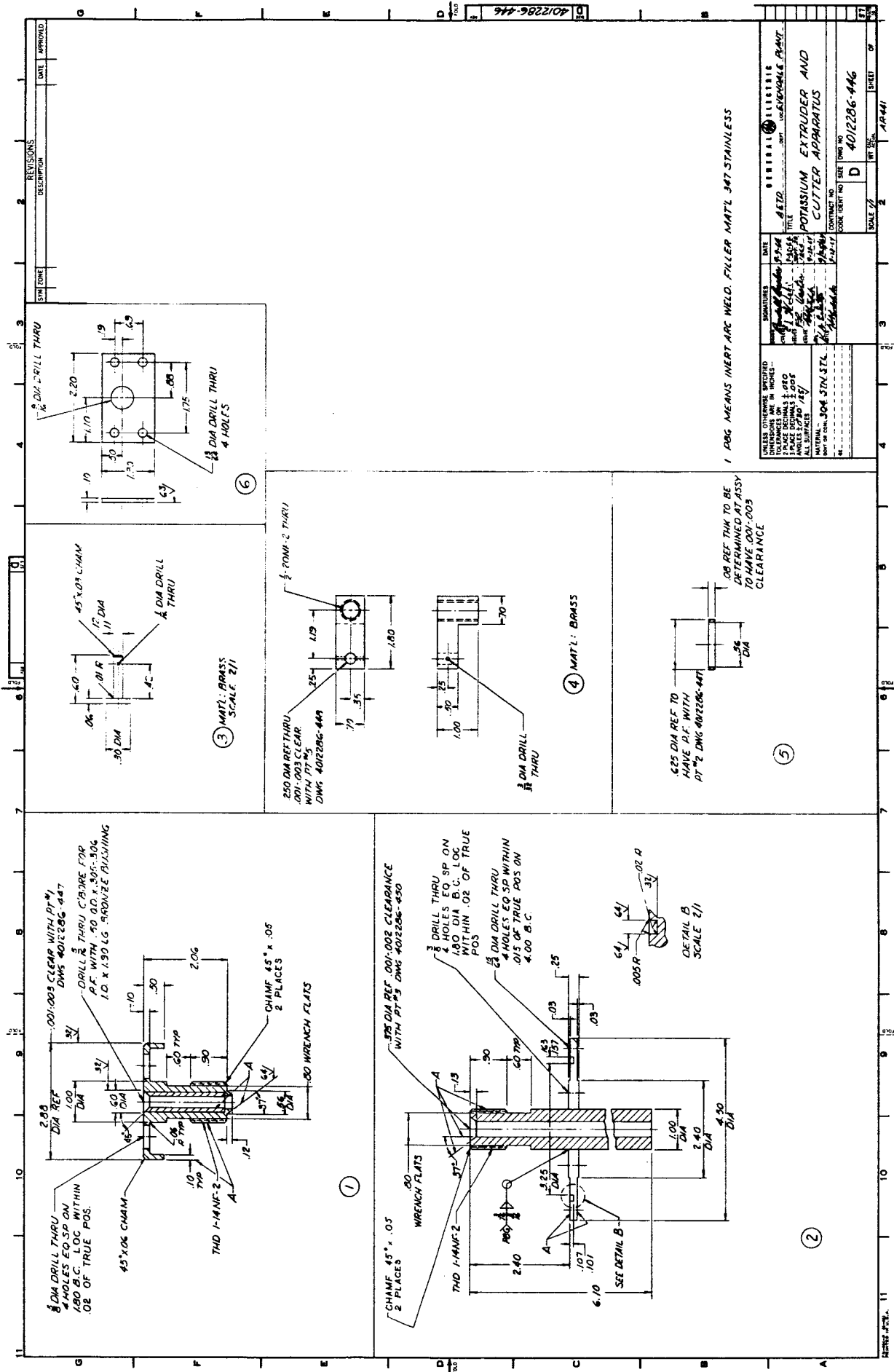




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AIRCRAFT ENGINEERING TITLE: POTASSIUM EXTRUDER AND CUTTER APPARATUS CONTRACT NO. 4012286-444 SCALE: 1/1 SHEET 1 OF 1	
DATE: 1-1-44 DRAWN BY: J. B. WILSON CHECKED BY: J. B. WILSON APPROVED BY: J. B. WILSON	CONTRACT NO. 4012286-444 SCALE: 1/1 SHEET 1 OF 1





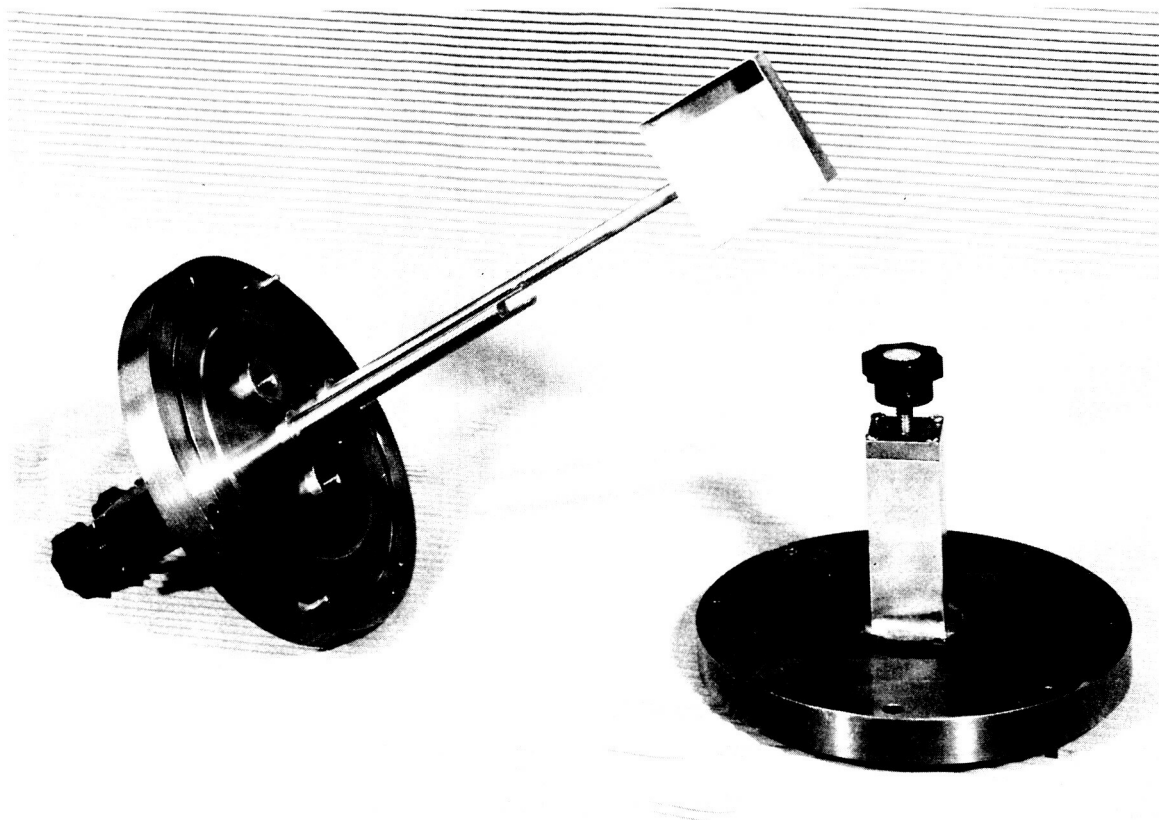


FIGURE 10 Extruder End Plates with Bellows-Sealed Activator Rods

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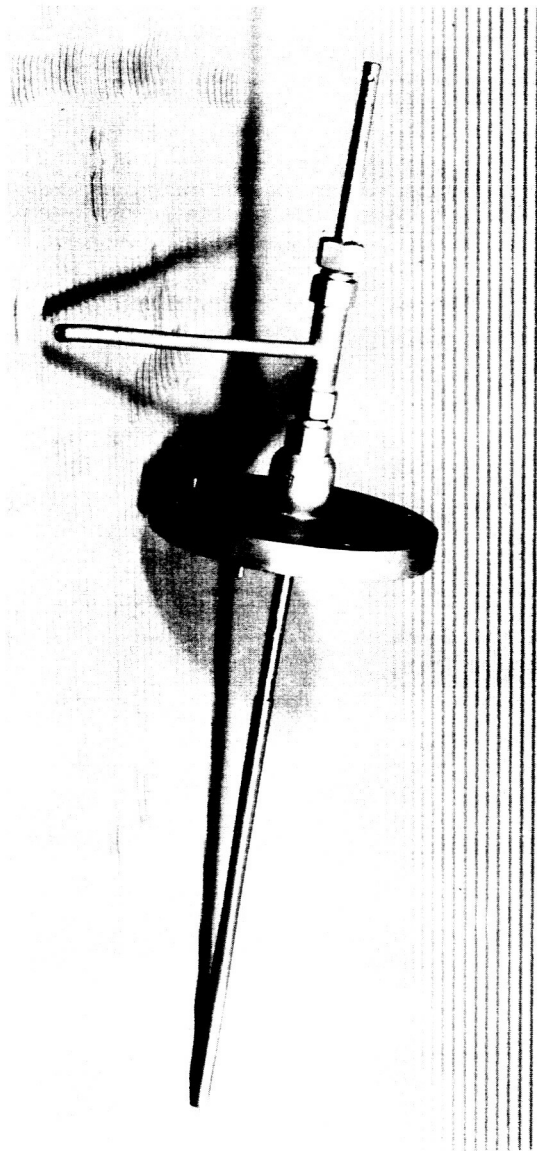


FIGURE 11 Double Vacuum Feed-Through With Extruder Rod

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A view of the oxygen measuring system is shown in Figure 12, and a schematic drawing of the Brady apparatus in Figure 13. The photograph in Figure 12 shows the apparatus exactly as it is during normal use, while the schematic shows it with the coulometric calibration cell in place. This is discussed in Section III, A.

A flow-through 1 cm absorption cell (Figure 14) with parallel sides is used, and absorption measurements are made with a Model 139 Hitachi-Perkin Elmer spectrophotometer. The results are recorded on a Photovolt Linear/Log Varicord Model 43 chart recorder.

III CALIBRATION OF SYSTEMS

A. Calibration of the Oxygen Measuring System

The Brady apparatus was calibrated by generating known amounts of oxygen in a coulometric cell attached to the helium inlet of the Brady apparatus. A known constant current passing through the cell (containing 10% H_2SO_4) for a given period of time yields a definite amount of oxygen. This amount, in accordance with Faraday's law, may be expressed by the equation:

$$\text{Micrograms Oxygen} = .08287 I \cdot t$$

Where I is expressed in milliamperes and t in seconds. Initially, some difficulty was encountered with the electrolytic cell shown in Figure 13 due to polarization and solution of both generated and atmospheric oxygen in the electrolyte. These difficulties were overcome by modifying the cell as shown in Figure 15. As a result of these modifications, dissolved oxygen could be efficiently removed from the electrolyte by bubbling helium through it. The fine glass frit, through which the helium entered the cell, was so positioned that a steady stream of helium passed over the anode, thus removing any oxygen bubbles which had a tendency to cling to it after the current was stopped. Difficulties in current regulation due to polarization were overcome by a current regulating circuit shown in Figure 16. By means

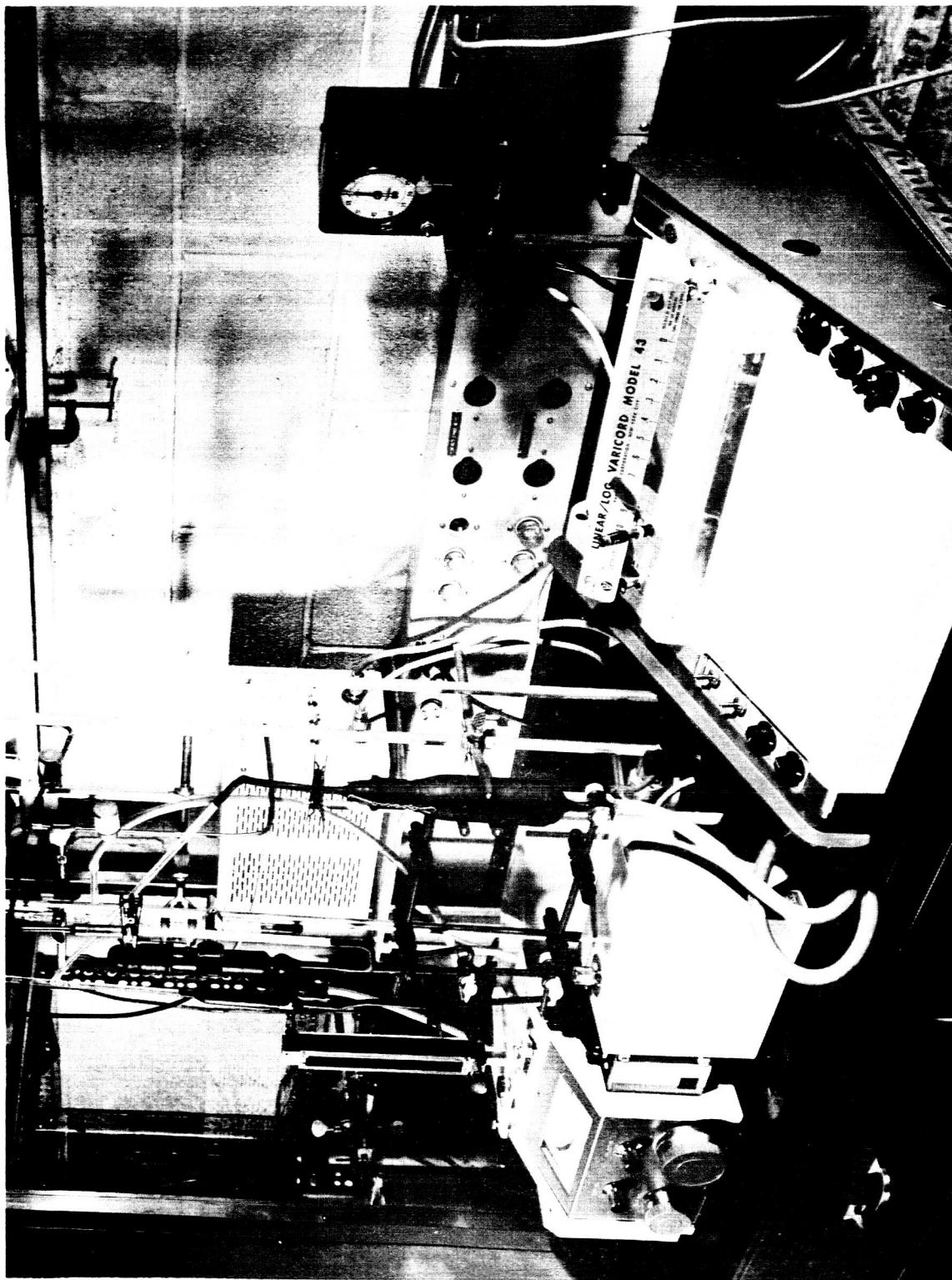


FIGURE 12 Oxygen Measuring System for the Determination of Oxygen in Potassium Metal

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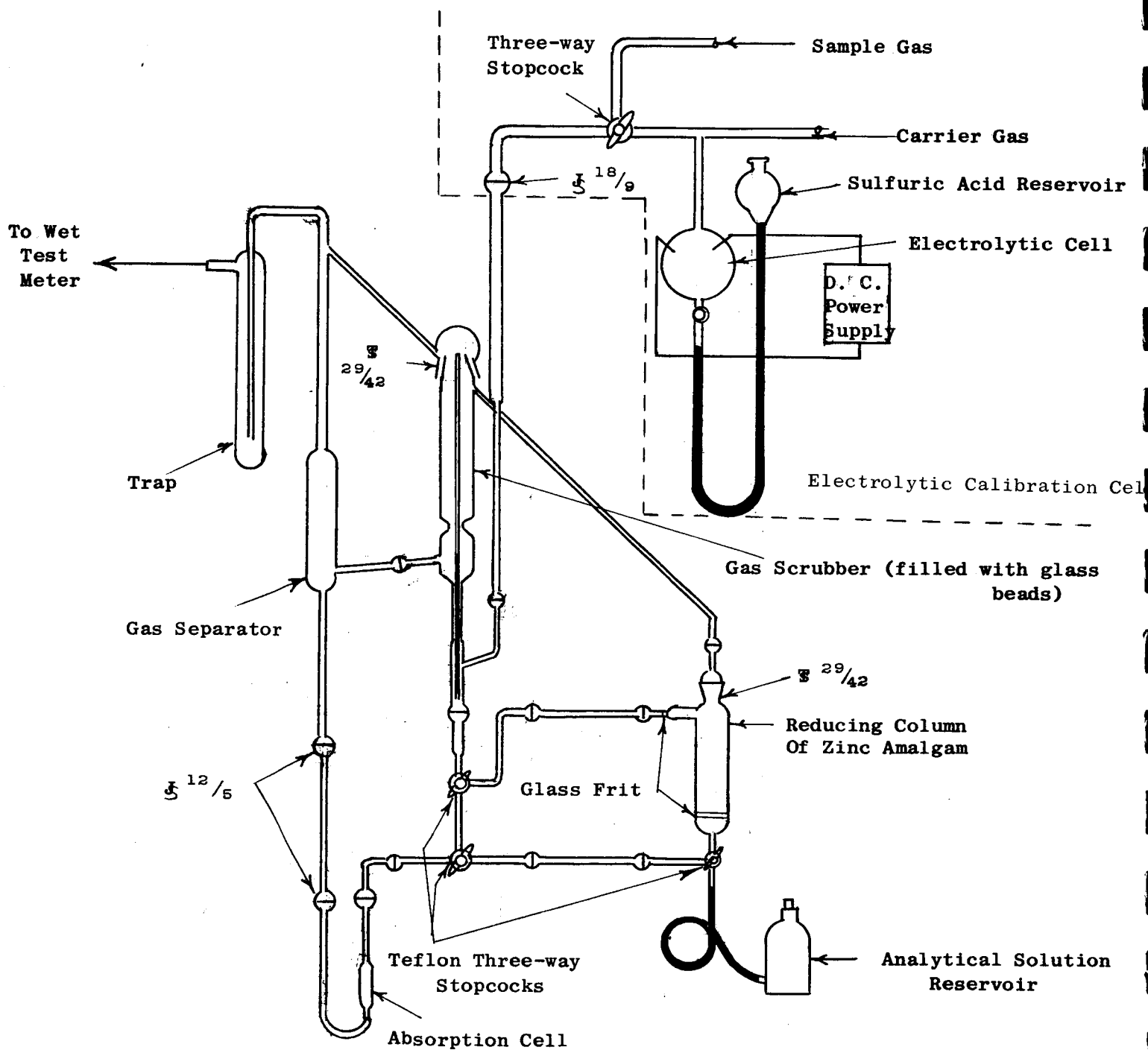


FIGURE 13 Diagram of Modified Brady Apparatus



FIGURE 14 Absorption Cell for Brady Apparatus

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FIGURE 15 ELECTROLYSIS CELL
FOR BRADY APPARATUS

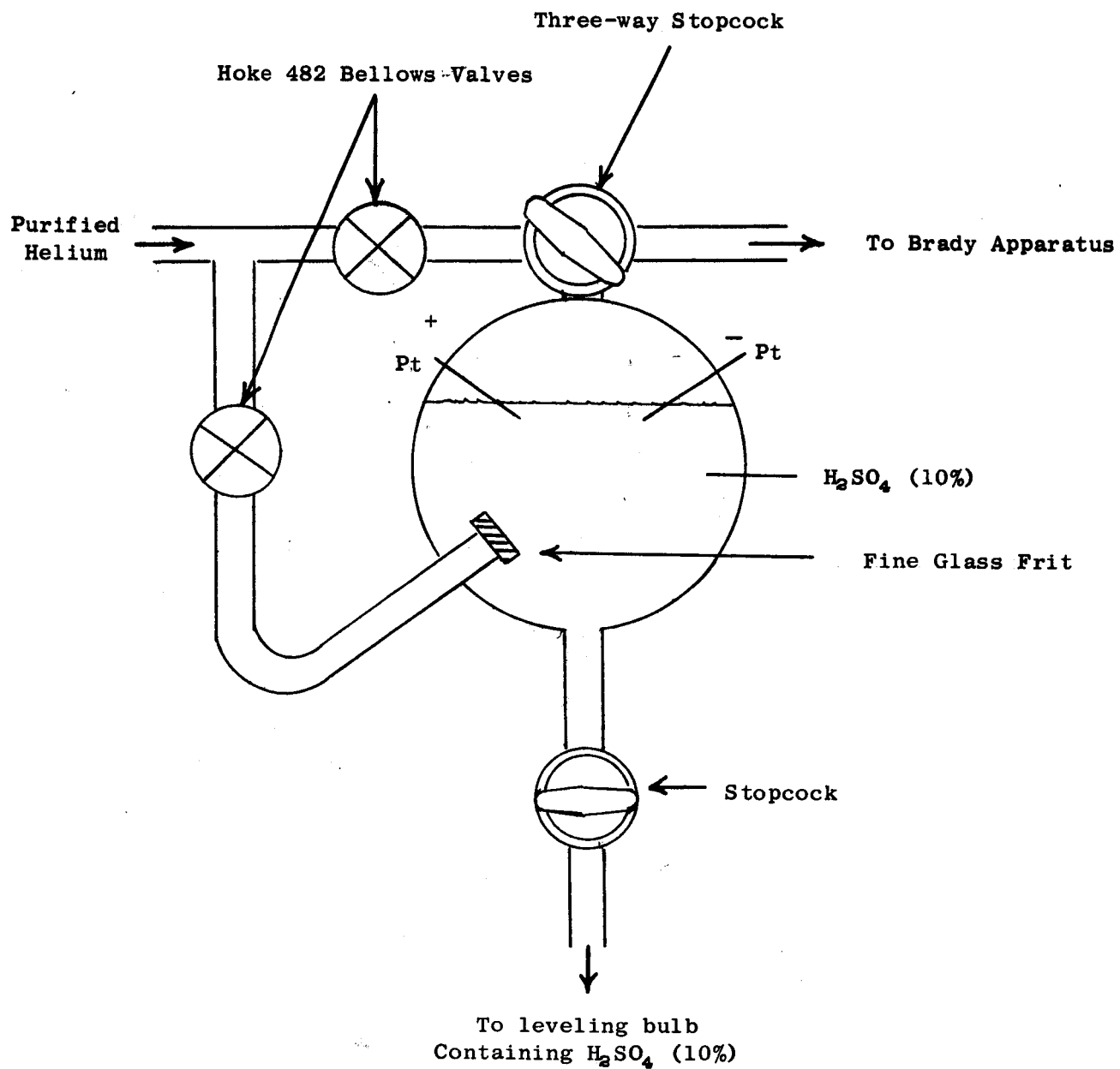
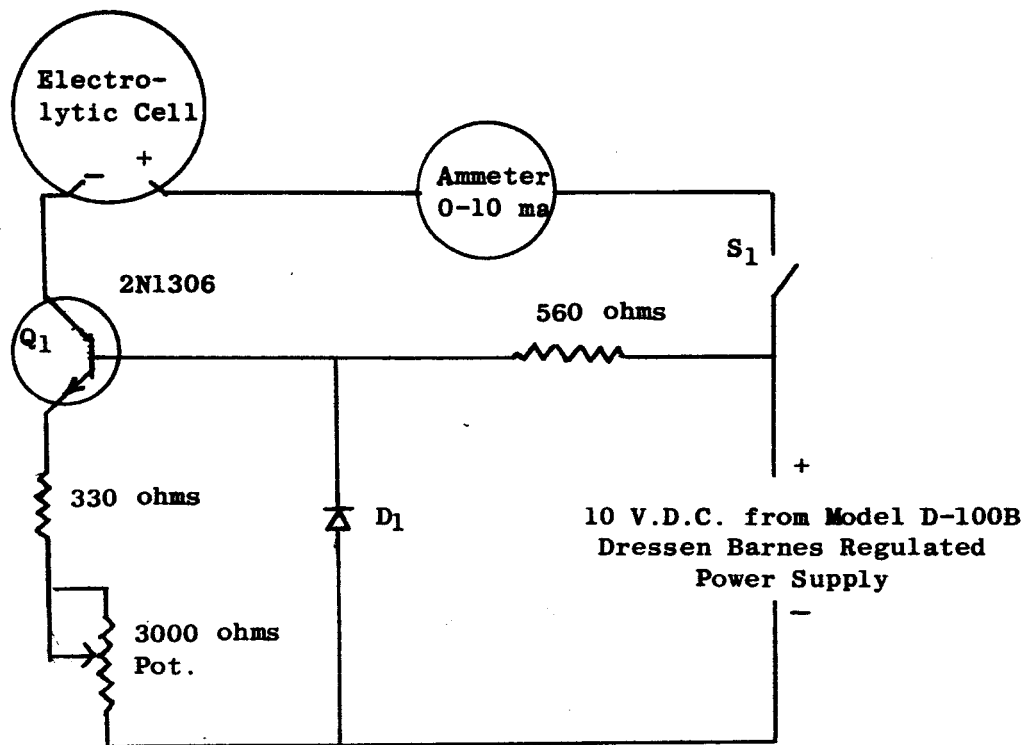


FIGURE 16 CURRENT REGULATING CIRCUIT FOR ELECTROLYSIS CELL
ON BRADY APPARATUS



of the 3000 ohm potentiometer, the milliammeter could be preset to a given current reading. Thereafter, whenever the circuit was closed, a precise current flow was automatically maintained regardless of the degree of electrode polarization in the cell. Current measurements were made with a Simpson Model 37 milliammeter reading from 0-10 milliamperes. The meter was calibrated by measuring the potential drop across a standard one ohm resistance placed in series with it. Voltage measurements were made with a Type K Leeds & Northrup potentiometer. The resulting meter calibration curve is shown in Figure 17.

As can be seen from Table I, most of calibration points were obtained with a generating current of 6.10 ma. At this current level, oxygen is being generated at a rate of about 0.5 micrograms per second. In order to be certain that none of the generated oxygen was passing through the Brady without being absorbed in the reagent solution, a number of tests were also run using a generating current of 2.00 ma. The fact that both sets of points fall on the same curve is regarded as proof that all of the oxygen is recovered at the normal flow rate (108 cc/min). The results are displayed graphically in Figure 18. For purposes of clarity, values up to 90 micrograms oxygen are plotted on a larger scale in Figure 19.

The procedure employed in the calibration of the Brady apparatus was as follows:

The level of the 10% H_2SO_4 in the electrolytic cell was raised so that the two electrodes were just covered. By means of the Hoke #482 bellows valves, the helium flow was regulated so that a steady stream of helium bubbles flowed through the electrolyte while, at the same time, some helium flowed across the top of the cell (see Figure 15). The three-way stopcock was set in a position so that all parts were interconnected. The total helium flow through the Brady apparatus was finely adjusted by means of the needle valve in the Matheson No. 602 flowmeter attached to the exit end of the Brady apparatus. The flow reading on the R-2-15-D flow tube was held at 70 mm (108 cc/minute).

FIGURE 17 MILLIAMMETER CALIBRATION CURVE

Simpson Model 37 Ammeter
Serial No. 19320

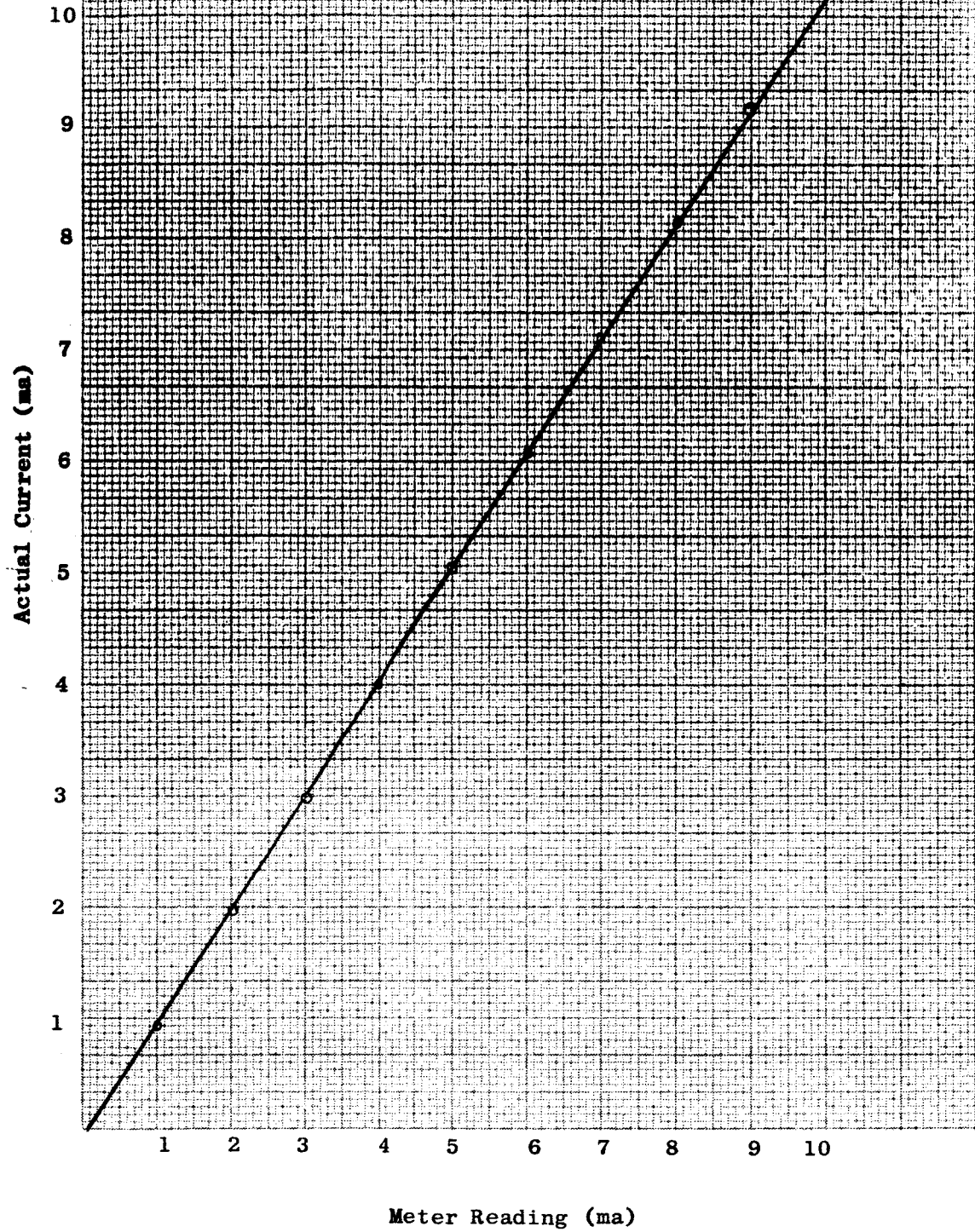
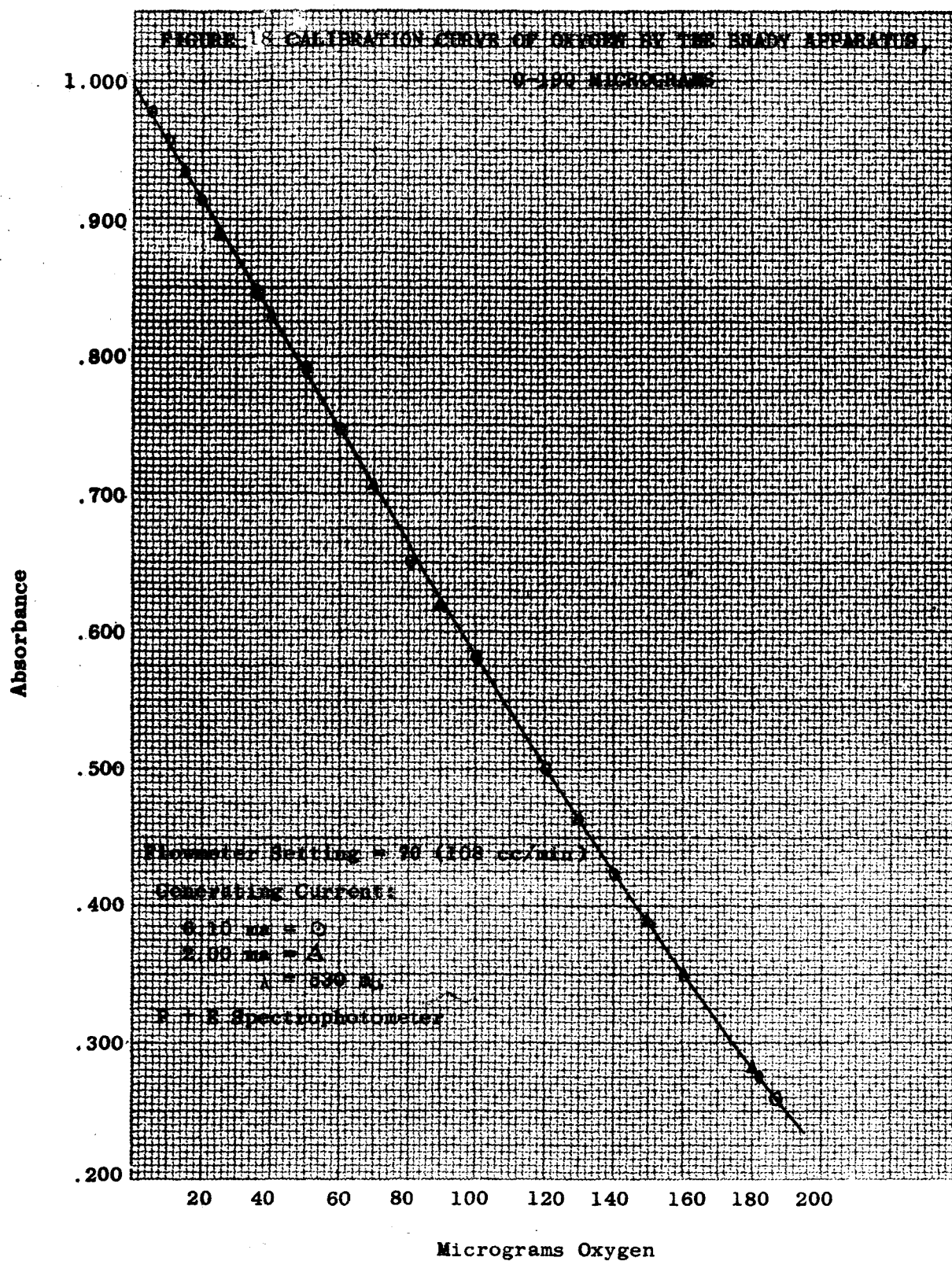
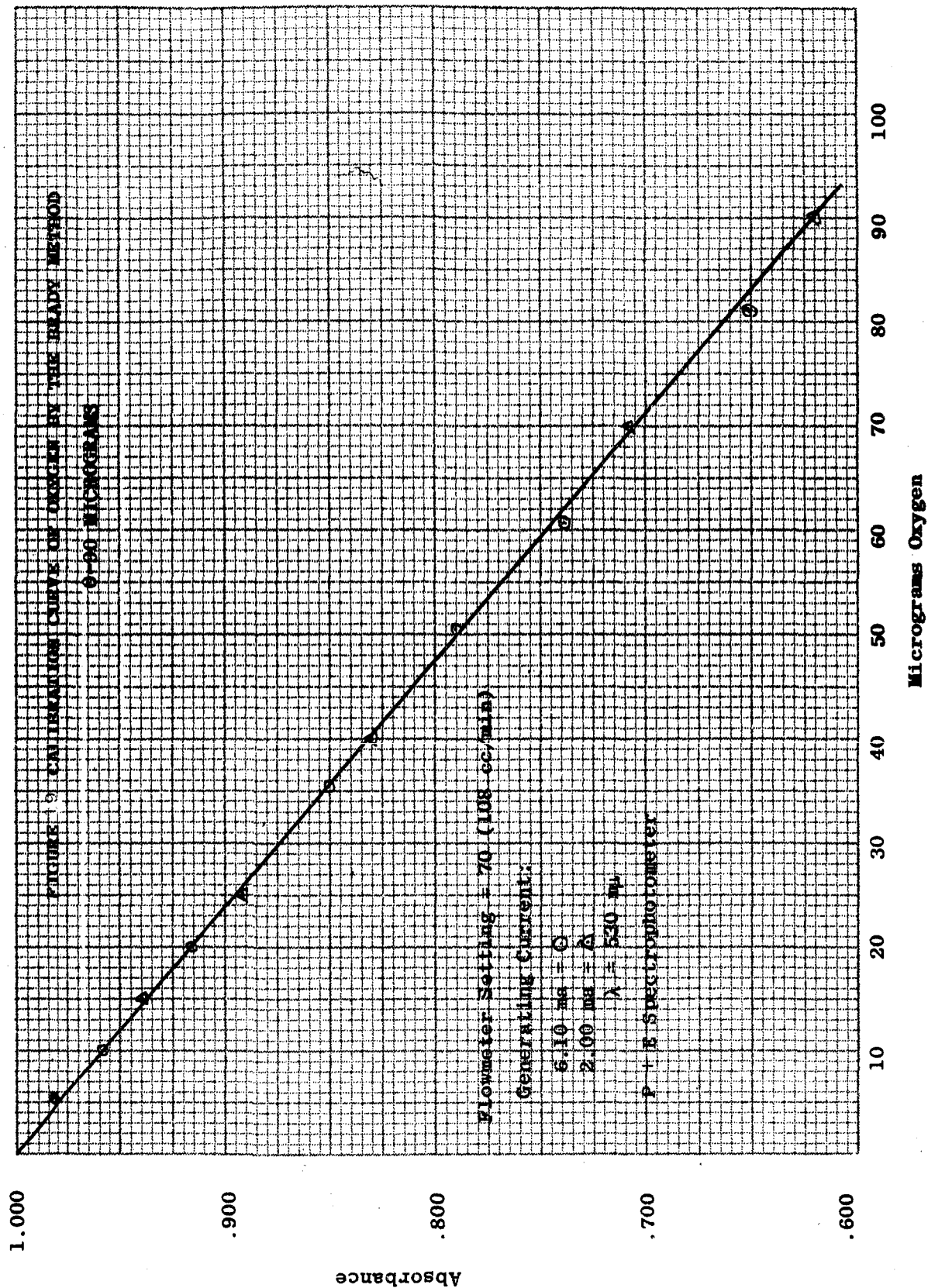


TABLE I
CALIBRATION DATA - BRADY APPARATUS

<u>Micrograms Oxygen</u>	<u>Absorbance</u>	<u>Generating Current (ma)</u>
5.06	.984	6.10
10.1	.962	6.10
14.9	.940	2.00
20.2	.915	6.10
25.0	.892	2.00
35.4	.851	6.10
40.1	.830	2.00
50.6	.790	6.10
60.6	.742	6.10
70.4	.708	2.00
80.9	.650	6.10
90.0	.621	2.00
101.1	.574	6.10
121.2	.500	6.10
130.0	.465	2.00
141.6	.420	6.10
150.0	.388	2.00
161.9	.347	6.10
180.0	.283	2.00
182.0	.274	6.10
187.0	.258	6.10





While the flow was being regulated, the solution in the Brady apparatus was circulated through the zinc amalgam reducing column. The Perkin-Elmer Spectrophotometer and the Varicord Model 43 chart recorder were turned on and the absorbance monitored. With the slit set at about 0.12 mm, the absorbance reached a maximum absorbance value of about 1.000 or slightly less.

After the absorbance reached its maximum value and the gas flow had attained a steady state, the Teflon stopcocks of the Brady apparatus were adjusted so as to by-pass the reducing column. By suitable manipulation of these stopcocks, the level of solution in the gas separator was adjusted to the reference mark. (It is important that this be done with the flow regulated exactly at 70 mm on the flowmeter so as to obtain the same quantity of reagent solution each time. Once the level has been set and the stopcocks closed, changes in the flow rate do not affect the quantity of solution in the analytical section.)

The chart recorder trace was observed for a period of about thirty minutes. During this time, if there were no leaks in the system, the absorbance would not change noticeably. The decrease in absorbance during a 45-minute blank run seldom exceeded 0.001 absorbance unit. At this level, the blank is negligible since one microgram of oxygen produces an absorbance change of about 0.005 units.

After the blank level (if any) was determined, the absorbance reading on the chart recorder was noted. Then the power supply to the electrolysis cell was actuated, noting the time interval with a stopwatch. After purging for about 30 to 45 minutes (depending on the amount of oxygen generated), the chart recorder trace leveled off at some lower absorbance value. The difference in absorbance, corrected for any blank, was subtracted from 1.000 and plotted against the micrograms of oxygen generated.

Following a calibration run, the solution in the Brady apparatus was regenerated by circulating through the reducing zinc amalgam column. At the lower oxygen levels, several runs could be made before the solution was regenerated. The absorbance was not allowed to drop below about 0.3 during the course of a run.

Because of the excellent stability of the Hitachi Perkin-Elmer spectrophotometer and Varicord chart recorder combination, the absorbance in the range of 0-1.000 can be estimated to within 0.002 absorbance units with considerable confidence. This accuracy, coupled with the fact that the sample cuvette is fixed and that only differences in absorbance, rather than absolute absorbance values need be measured, indicate that the relative error should be very small by spectrophotometric standards--perhaps less than one percent.

B. Calibration of Weight of Potassium Sample by Extruder Turns

In order to correlate the number of extruder turns to the weight of potassium extruded, the following procedure was used:

Samples of potassium (from NASA, Cleveland) were obtained in nominal 3/8" OD x 6-3/4" stainless steel tubes having one flared end. The tubes are illustrated in Figure 20. After removal of the end caps, a tube was placed in the extruder in the normal fashion. With the extruder under high vacuum (4×10^{-6} torr), a small number of turns was first made to expose the oxidized end. This exposed length was then cut off with one of the two cutting wires and discarded into the waste pan. The sample piece was then extruded, cut off, and positioned in the center of the extruder. The sizes of the potassium samples corresponded to randomly chosen extruder turns in the range of 5 to 20 turns. The ball valve, connecting the extruder and the reaction cell (which had been evacuated previously by means of the rough vacuum system) was opened and the cutting wire heated (using the 3V battery), causing the sample to drop into a 150 ml glass beaker contained within the reaction cell. The ball valve was then closed and the reaction cell brought to atmospheric pressure.

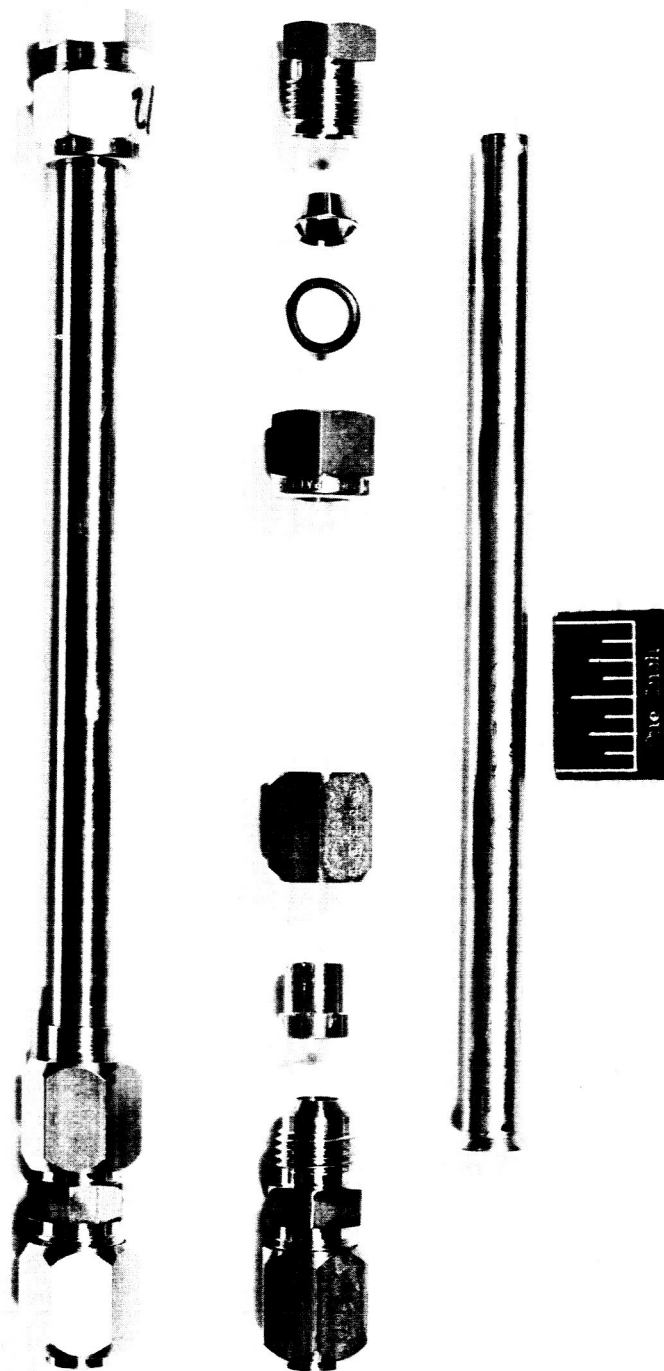


FIGURE 20 NASA Potassium Sample Tubes

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After removal from the cell, the potassium was immediately transferred to a tared 100 ml platinum dish and covered with hexane. The potassium was then carefully reacted by dropwise additions of ethanol to convert it to the alkoxide. Any potassium adhering to the glass beaker was treated similarly and then transferred quantitatively to the platinum dish.

After completion of the reaction with ethanol, the sample was treated with an excess of concentrated hydrochloric acid to convert all of the potassium to the chloride. The organic solvents then were removed by evaporation, using infrared lamps. The platinum dishes containing the chloride were placed in a drying oven at 120°C for at least one hour, then the dried samples were cooled to room temperature in a desiccator and weighed as potassium chloride. Subsequently, the equivalent amount of potassium was calculated. The results are shown in Table II and Figure 21. Including the point at 17 turns, one can expect a weight determination with less than 2% error.

IV ANALYTICAL RESULTS

A. Analysis of KBrO_3 Additions

During the third quarter of work on this project, an attempt was made to evaluate the accuracy of the method by analyzing synthetic samples containing known amounts of oxygen added in the form of potassium bromate. Generally, the results were inconsistent and low recoveries were frequently obtained. It was noted, however, that under certain specific conditions ⁽⁸⁾ essentially complete recovery could be obtained. It was surmised that incomplete recoveries were the result of either the failure to remove dissolved oxygen from the BrF_3 ; the formation of stable oxides of bromine; or a combination of these phenomena.

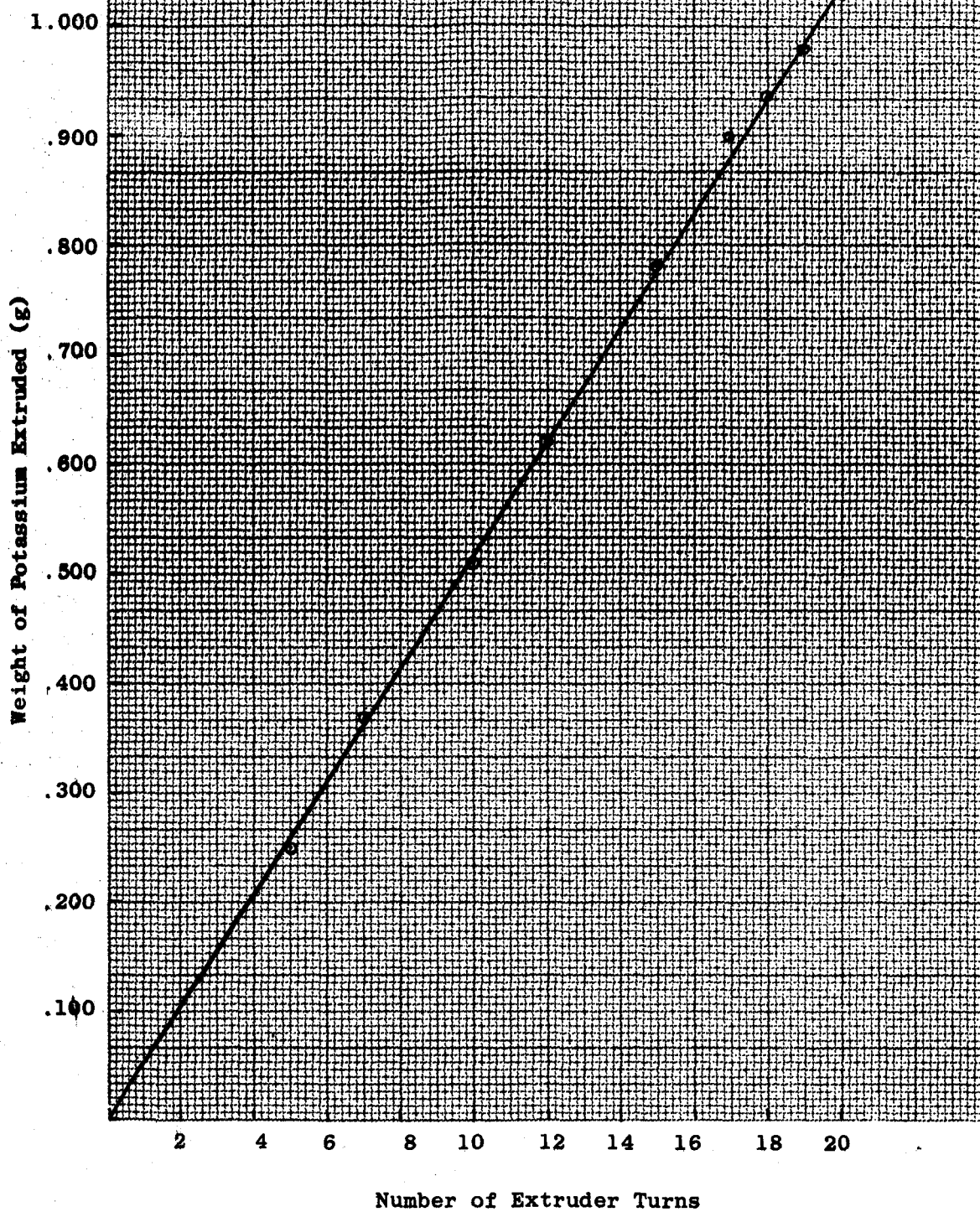
In order to minimize these possibilities, the following conditions of analysis were set up and adhered to in all subsequent determinations:

TABLE II
DETERMINATION OF SAMPLE WEIGHT OF POTASSIUM BY EXTRUSION*

<u>Extruder Turns</u>	<u>Wt. of Potassium (g)</u>
5	0.2543
7	0.3692
10	0.5124
12	0.6231
15	0.7800
17	0.9007
18	0.9365
19	0.9814
20	1.0376

*Obtained by converting K to KCl and weighing.

FIGURE 21 DETERMINATION OF SAMPLE WEIGHT OF POTASSIUM
BY EXTRUSION



1. The volume of BrF_3 in the reaction cell was closely controlled and held at about 25 ml, just sufficient to cover the opening of the helium dip-leg inlet.
2. Since BrF_3 forms no thermally stable bromine oxides⁽⁴⁾, the cell temperature was regulated at 70°C by means of a water bath. It was reasoned that this should tend to minimize the solubility of oxygen as well as speed up the dissociation of bromine oxides.

The analytical procedure for the KBrO_3 additions was the same as that used for potassium metal (see Section IV, B) except that the samples were reacted under a positive pressure of helium instead of vacuum. That is, after the sample had been dropped into the reaction cell under vacuum and at about liquid nitrogen temperature, the cell was pressurized with helium and then purged through the Brady to establish the helium blank rate. The cell was then warmed to $+70^\circ\text{C}$ and the change in absorbance, due to sample oxygen noted. In this way, the "apparatus blank" (to be discussed later) was avoided.

The oxygen recoveries obtained are listed in Table III. Some difficulties were encountered due to flaking of the dried KBrO_3 off of the copper sheets on which the material was introduced into the apparatus. This may account for the several low results obtained; however, the average oxygen recovery of all samples run under the above-mentioned conditions was 92.1%.

The samples were prepared from a standard solution containing 1.7397 grams of dried reagent grade (assay = 99.8% KBrO_3) potassium bromate per liter. Aliquots of this solution were then measured onto 1/2 inch squares of previously prepared copper sheet. Aliquots were measured with a syringe microburet Model SB 2 manufactured by the Micro-Metric Instrument Company, using a No S1/4LT syringe calibrated to deliver 0.200 microliters per division of the micrometer dial. After dispensing, the solutions were evaporated to dryness under infrared lamps and then baked for one hour at 120°C in a drying oven.

TABLE III

OXYGEN RECOVERY FROM KBrO_3 ADDITIONS

<u>Oxygen Content</u> <u>(micrograms)</u>	<u>O_2 Recovered</u> <u>(micrograms)</u>
40	27.5
50	47.7
60	53.3
60	58.3
80	73.3
100	99.0
$\Sigma = 390$	$\Sigma = 359.1$

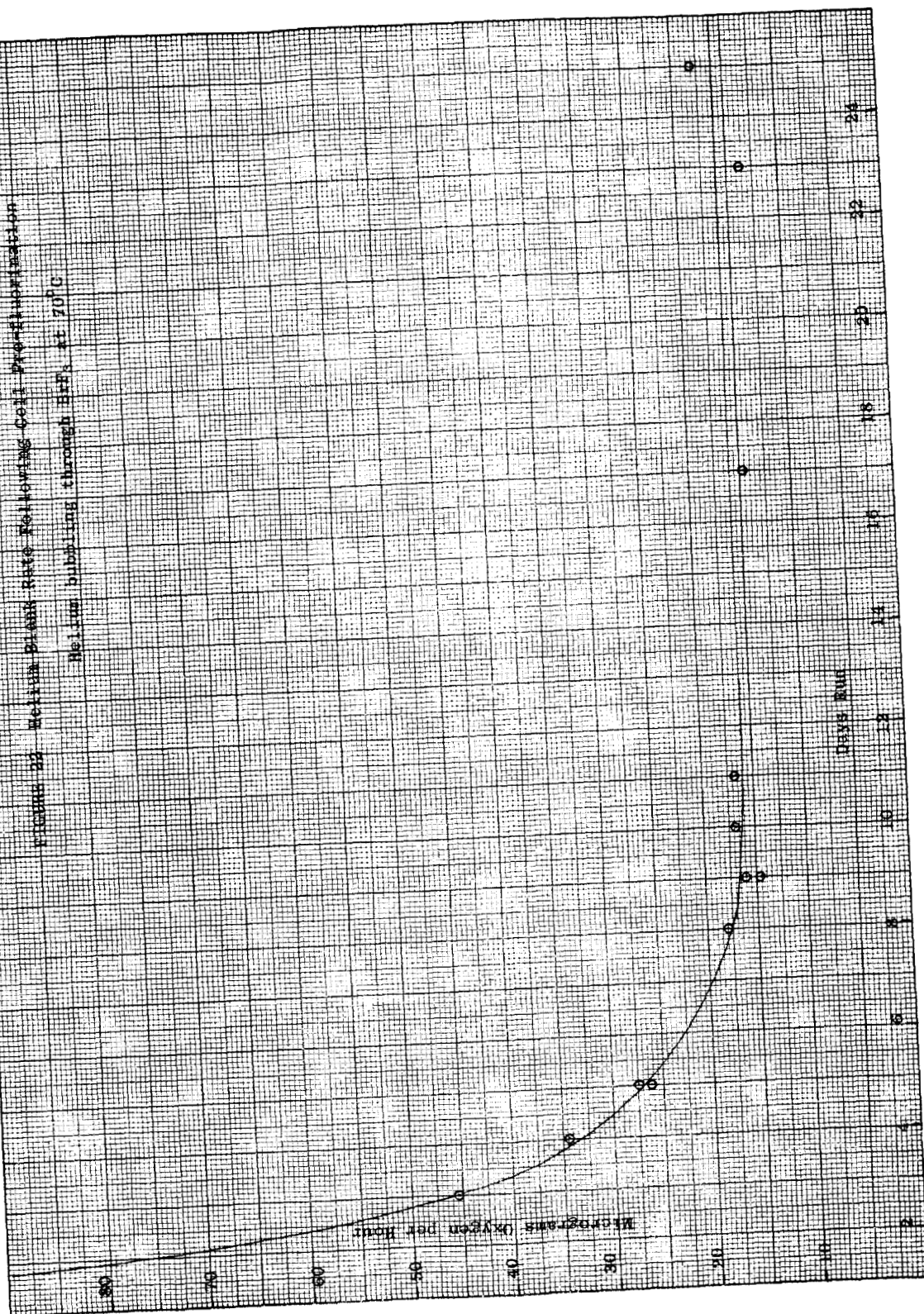
% Recovery = 92.1

The top section of the extruder which normally contains the potassium tube was removed and the sample bearing copper sheet was lowered into the extruder and allowed to rest upon the ball of the Hills-McCanna ball valve. The extruder opening was then closed with a 3/8" thick pyrex window and the extruder pumped down. Opening the ball valve then dropped the sample (which could be observed through the window) into the reaction cell.

It was noted that the helium blank, with the reaction cell at 70°C, was approximately two to three times that obtained with the cell and its contents at room temperature. The purified helium coming from the NaK bubbler contains about 0.2 ppm of oxygen. After passing through the analytical apparatus, bubbling through BrF₃ at room temperature en route, the resulting helium blanks generally measures between 5 and 10 micrograms of oxygen per hour. The average of the six helium blanks obtained during the analyses of the samples listed in Table III with a cell temperature of 70°C was 18.03 micrograms per hour. The dependence of the blank rate upon cell temperature was later confirmed by observing the blank rate at several temperatures during pre-fluorination of the reaction cell following clean-out of the cell and the addition of fresh BrF₃. With the reaction cell at 70°C, the helium blank rate was 34.3 micrograms per hour. Lowering the cell temperature to about 25°C caused the blank rate to drop immediately to about 9 micrograms per hour.

A primary consideration is that the blank should remain relatively constant. That this condition is met can be seen from the data plotted in Figure 22. Here the helium blank rates obtained during the course of a number of potassium analyses was plotted versus time measured from the date on which the reaction cell was cleaned out and recharged with fresh BrF₃. The helium blank levels off at about 16.0 micrograms per hour; a value in fair agreement with that obtained during the analysis of the KBrO₃ standards (18.03 µg/Hr). As can be seen from the curve, approximately one week of prefluorination is required for the helium blank rate to reach its lower

FIGURE 22 Helium Blank Rate Following Cell Sterilization
Helium bubbling through HEPs at 70°C



limit. Unless the samples to be analyzed are quite low in oxygen; however, it is not necessary to wait this long since the rate of change is quite slow after the third day (less than $0.5 \mu\text{g}/\text{Hr}$). Small variations in the day-to-day blank rate may be due to slight changes in operating conditions and generally do not exceed five micrograms per hour from one day to the next. During the course of any one analysis, the change in blank rate is therefore negligible. The average time required for analysis of a potassium bromate sample is 145 minutes while a sample of potassium metal can be analyzed in 90 minutes. Possible reasons for this time discrepancy may be the much greater reactivity of the potassium metal, and the fact that the metal sample is reacted under a partial vacuum, while the bromate standard is reacted under a positive pressure of helium.

B. Potassium Analyses

The results of oxygen analyses of potassium metal samples are listed in Table IV. The only sample for which comparative data by other analytical methods is available is GE-137. This sample was analyzed by both neutron activation and mercury amalgamation; the results are also listed in Table IV. While no definite conclusions can be drawn from the rather limited data presented here, it would appear that the results obtained by the BrF_3 method are highest. For the reasons mentioned in the introduction to this report one might very well expect the values obtained by this method to be higher than those obtained by the mercury amalgamation method - particularly if the potassium were to contain appreciable amounts of transition metal oxides. It was hoped that the BrF_3 results might be in reasonable agreement with those values obtained by neutron activation; however, these lie in between the results obtained by the other two methods and are somewhat closer to the amalgamation results. In addition, the rather broad limits of error of the neutron activation values render these latter even more ambiguous.

Considerable sampling problems were encountered, due primarily to the presence of oxides which formed around the sample tube openings during loading operations. At first, attempts were made to remove the deposits manually but this only aggravated matters and prolonged loading time.

TABLE IV
OXYGEN ANALYSES OF POTASSIUM METAL
BY THE BrF₃ METHOD

Sample Designation	<u>L-10</u>	<u>L-20</u>	<u>J-16</u>	<u>K-21</u>	<u>GE-137</u>
	288 ppm	341 ppm	147 ppm	239 ppm	124 ppm
	329	348	184	240	104
	304	351	186	241	127
	284	350			
	274	339			
Average	296	346	172	240	118
Standard Deviation	21.5	5.4	22.0	1.0	12.5
Coefficient of Variation	7.27%	1.56%	12.8%	0.41%	10.6%

Mercury Amalgamation O₂ Analysis of GE 137:
(E. Dotson, et.al.)

53.7 ppm
52.4
44.3
50.8

Average 50.3 ± 7.6 ppm

Neutron Activation O₂ Analysis of GE 137:
(General Dynamics)

83.5 ppm
73.1

Average 78.3 ± 23.5 ppm

The tubes were loaded into the extruder and the extruder pumped down as quickly as possible in an attempt to minimize oxide formation. Pieces of waste potassium were then extruded and cut off in an effort to remove oxide deposits around the inside edge of the sample tubes. Unfortunately, this was never entirely successful and close examination always revealed some remaining oxide; even though more could be seen on the freshly extruded potassium. Initial high results on all samples were therefore attributed to this source of contamination. In the case of J-16 and L-20, these initial values were so high as to exhaust the reagent in the Brady apparatus. Following the extrusion of sufficient potassium, the results leveled off; but considerable sample material was wasted in the process. In the case of GE-137, a large cavity at the mouth of the tube and extending up into it further reduced the amount of potassium available and thus, the number of samples which could be run. After the three results listed in the table, four samples, on J-16 had been obtained, a segment of potassium with a black, rather flaky surface was extruded. This proved to be extremely high in oxygen and the remainder of the tube was discarded.

In order to determine whether or not the relationship between sample weight and oxygen content was linear, sample weights for L-20 and K-21 were varied. That the relationship is indeed linear can be seen from a plot of the results in Figures 23 and 24. The scattered low values obtained for K-21 were attributed to an insufficient amount of BrF_3 in the reaction cell, in which case the helium dip-leg may not have extended beneath the surface of the liquid. Since the liquid level cannot be observed visually during the course of an analysis, it must be determined indirectly by observing the helium pressure in the manifold. When the reaction cell is evacuated, the BrF_3 frozen with liquid nitrogen, and the helium supply valve leading to the manifold closed; then opening the dip-leg helium inlet valve will only cause the manifold pressure to drop about two pounds if the frozen BrF_3 level is high enough to close off the opening of the dip-leg. If the level is quite low the helium will flow into the reaction cell and the manifold pressure will drop to about two inches of mercury.

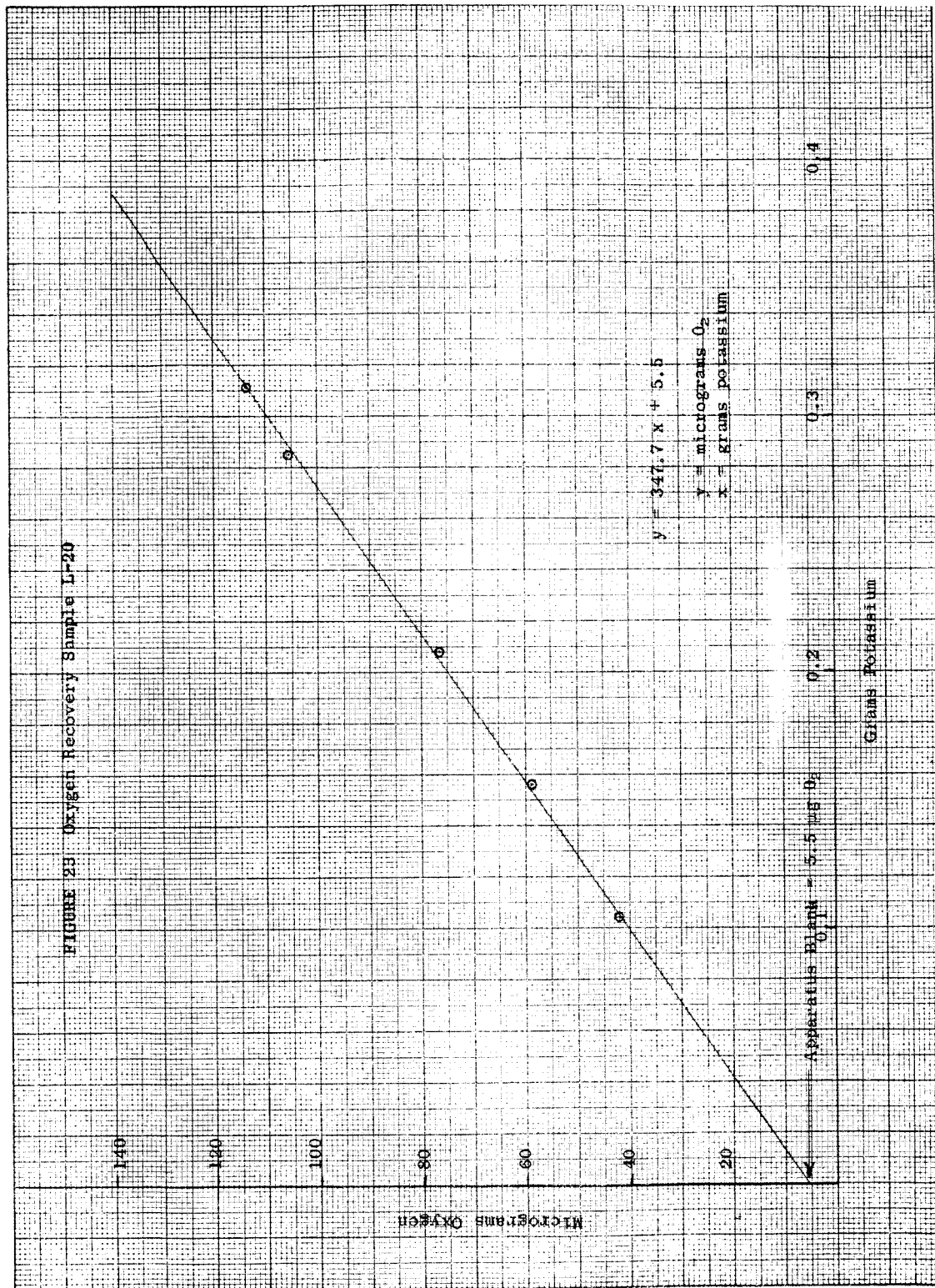
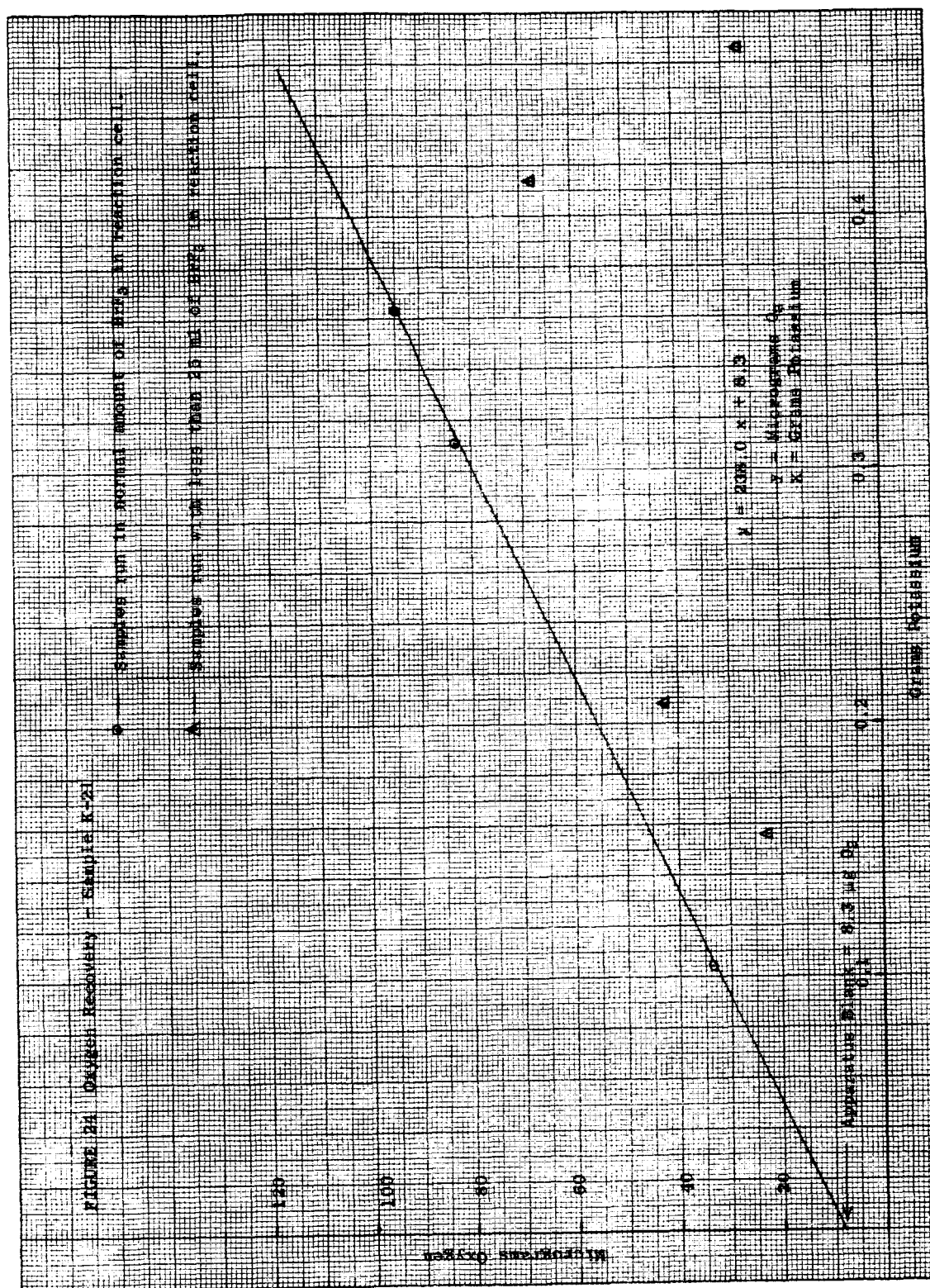


FIGURE 2A Oxygen Recovery - Sample K-21



When this occurs, during the initial pump-out preceding a day's run, more BrF_3 (usually about 5 ml) is added to bring the level up to normal. Unfortunately, if the BrF_3 is just touching the dip-leg, the opening may be plugged completely or sufficiently to cause only a very gradual drop in manifold pressure. Conversely, fissures in the frozen BrF_3 , even when a sufficient amount is present, may permit helium to flow into the cell slowly. In such cases it is difficult to determine the exact BrF_3 level necessary in order to duplicate the conditions under which complete O_2 recovery was obtained from bromate additions.

Of the K-21 analyses plotted in Figure 24, the 0.363 gram sample was the first run. Following this determination all the low values were obtained. Manifold pressure readings, as described above, were indeterminate during the course of these analyses; however, very gradual drops in pressure had been observed before without affecting the results. An additional 5 ml of BrF_3 were then added to the reaction cell and the values at 0.311 and 0.104 grams of potassium were obtained. At this point the supply of potassium was exhausted and no further analyses could be conducted to verify the hypothesis that the low values were the result of incomplete recovery due to insufficient BrF_3 . Test results on the sample must therefore remain suspect.

The curves plotted in Figures 23 and 24 intercept the y axis at 5.5 and 8.3 micrograms of oxygen, respectively. These values may be considered as representing the "apparatus blank" of the equipment and agree well with individually measured apparatus blanks. A total of six such blank runs were made, their average value being 7.8 micrograms of oxygen. The reagent blank or "helium blank rate" as it is referred to in this report is determined separately and individually for each sample, and represents the amount of oxygen present in the effluent helium stream after it has passed through the entire analytical system, being bubbled through the BrF_3 reaction cell at 70°C . The method of handling the helium blank rate is described below in an account of the analytical procedure used for potassium samples.

1. Load the sample tube of potassium into the extruder and pump down immediately. The loading operation should be performed as quickly as possible so as to minimize contamination. After the pressure in the extruder is less than 3×10^{-6} torr the analysis may begin.
2. While the extruder is pumping down, chill the cold traps of the rough vacuum system with liquid nitrogen. After the traps are cold, slowly open the valve between the monel and the glass traps. If the system has been pumped out previously, the pressure at the pump inlet should not exceed about 200 microns before dropping rapidly to about 5 microns. The liquid nitrogen level in the monel trap should be maintained at not more than one or two inches while pumping. Excess liquid nitrogen is not necessary to trap out BrF_3 or other condensable vapors and will only chill the trap flange to the point where the Teflon "O" ring will no longer be able to maintain an effective seal.
3. At this point, all analytical system valves (excluding vacuum system and helium purification system) should be closed, including the valve connecting the analytical system to the Brady apparatus. After the rough vacuum system has attained a pressure of about 5 microns, slowly open the vacuum valve to the reaction cell. The valve should be opened so that the vacuum pump gurgles slightly. Opening the valve too far or too rapidly may cause BrF_3 to be carried through the Monel freeze trap.

While the reaction cell is being pumped out, the valve connecting the reaction cell and the effluent cold traps may be opened and the cold traps pumped out simultaneously. After the mechanical pump has quieted down, open the valve to the vacuum system fully. While the pressure drops to about 5 microns, chill the reaction cell sufficiently to freeze the BrF_3 and continue cooling to about -50°C before removing the liquid nitrogen Dewar flask. While the BrF_3 in the reaction cell is still frozen, open the valve at the exit end of the second effluent

cold trap, thus permitting the line connecting the analytical system and the Brady apparatus to be evacuated. Before doing so, make certain the valve at the entrance of the Brady apparatus is closed lest solution from the Brady be drawn back into reaction cell.

4. After the reaction cell and effluent cold traps have been pumped down to about 5 microns, fill the Dewar flasks surrounding the effluent cold traps with pentane slush. After the traps have cooled to below -120°C , close the valve to the rough vacuum system and the valve between the roughing cold traps. Open the dip-leg helium inlet to check the BrF_3 level; the manifold pressure should drop about 2 pounds and then stop. Close the dip-leg helium inlet. Open the helium inlet to the reaction cell. The compound pressure gauge in the helium manifold (see Figure 1) will indicate a vacuum of about 25 inches of mercury. Admit pure helium into the entire system by slowly opening the valve connecting the manifold to the helium supply system. Regulate the flow by observing the manifold pressure gauge and the flowmeter on the helium tank regulator. Do not exceed about 1.2 cubic feet per hour. After pressurizing to a positive pressure of about 3 to 5 pounds per square inch, open the valve all the way.
5. The operation of the Brady apparatus is exactly the same as outlined in the Brady calibration procedure, section IIIA. During the preceding steps, pure helium from the NaK bubbler should be flowing through the apparatus and the flow rate, solution level, spectrophotometer and recorder adjusted in accordance with this procedure. The blank rate of the pure helium should be negligible - less than 2 micrograms per hour.

Close the valve supplying pure helium to the Brady and open the valve supplying gas from the analytical system. Adjust the flow rate to the proper level (about 70 mm on the flowmeter). Warm the reaction cell with warm water to thaw the BrF_3 . After the temperature exceeds 25°C , close the reaction cell helium inlet and open the inlet leading to the

dip-leg so that helium bubbles through the BrF_3 . Place the hot water bath (70°C) around the reaction cell.

Observe the blank rate on the recorder for about 60 minutes. The blank rate should level off to some constant value yielding a trace which is a straight line corresponding to about 10-20 micrograms of oxygen per hour.

6. After an acceptable blank has been obtained, again chill the cold traps in the rough vacuum system with liquid nitrogen. Close the valves connecting the Brady and the analytical system, the reaction cell and the effluent cold traps, and the dip-leg helium inlet to the reaction cell.

Employing the same procedure as outlined in Steps 2 and 3, pump out the reaction cell but do not pump out the effluent cold traps. After pumping out the cell, chill it with liquid nitrogen to about -150°C . Small amounts of helium admitted periodically into the reaction cell will improve the thermal conductivity and speed the cooling process. After the cell is cooled and a pressure of about 5 microns attained with the rough vacuum system, open the large ball valve to the extruder and close the valves of the rough vacuum system. The pressure in the extruder will rise momentarily perhaps as high as 10^{-4} torr but should drop immediately to about 2×10^{-5} torr. This is due primarily to helium from the reaction cell which cannot be pumped efficiently with the rough vacuum system. The prior blank-out of the cell will, of course, have removed all oxygen. There will also be some BrF_3 vapor in the extruder since the upper part of the reaction cell and adapter cannot be chilled adequately. This is evidenced by a noticeable odor of BrF_3 whenever the extruder is opened shortly after a run.

7. Extrude and cut two waste pieces of potassium, dropping them in the waste boat. Extrude the required amount of sample potassium and drop it into the reaction cell. Close the main ball valve.
8. Remove the liquid nitrogen Dewar from around the reaction cell and replace it with one containing warm water ($\sim 50^{\circ}\text{C}$). After the reaction cell has warmed to about 30°C , place the electrically heated hot water bath (70°) around the cell.
9. Open the helium inlet valve and, by means of the main helium supply valve (between the NaK bubbler and the helium manifold) slowly pressurize the reaction cell to about one pound positive pressure. Close the inlet valve to the cell and continue the pressurization by admitting helium through the dip-leg helium inlet. Pressurization will be complete at about 4-5 pounds pressure.
10. Stop the flow of pure helium from the NaK bubbler to the Brady apparatus. Open the reaction cell outlet valve and the Brady inlet valve adjusting the flow with the inlet valve to about 110 mm on the flowmeter. With the needle valve on the flowmeter, lower the flow rate to about 70 mm (108 cc/min). Note the time at which the flow through the Brady apparatus was begun on the chart recorder.
11. After about 5 minutes, the absorbance of the Brady solution should begin to decrease. Complete removal of oxygen from the reaction cell requires about 75 minutes. Oxygen recovery is considered complete when the recorder trace becomes a straight line with a slope identical to that attained during the blank-out procedure. The amount of oxygen recovered is then determined by extrapolating the straight line portion of the trace back to the time at which the flow through the Brady apparatus was begun. The final absorbance is taken as the point at which this line intersects the starting time. The difference between this

value and the initial absorbance represents the oxygen recovered from the sample plus the apparatus blank and is converted to micrograms of oxygen by subtracting this difference from 1.000 and reading the corresponding amount of oxygen from the calibration curve (either Figure 18 or 19). The apparatus blank may be determined by plotting the amounts of oxygen recovered from different size samples versus sample weight and noting they intercept; or, if insufficient sample is available, by running blank determinations (7.8 micrograms). The helium blank is automatically subtracted during the extrapolation process.

A typical absorbance plot produced by a potassium sample containing 51.3 micrograms of oxygen (including the 7.8 microgram apparatus blank) is reproduced in Figure 25. The vertical section at the bottom represents pure helium coming directly from the purification system; hence, there is no discernable change in absorbance. The flow of sample gas is begun at the point marked "Start flow". Somewhat less than 5 minutes later (chart speed = 12 inches per hour) the absorbance begins to drop and continues to do so for about 70 minutes. After this time the slope remains constant representing a helium blank rate of 16.9 micrograms per hour.

Up to 3.5 grams of potassium metal were analyzed in a 25 ml volume of BrF_3 with no significant loss of recovery. At this point, however, difficulties developed which were primarily mechanical in nature. Owing to the rather vigorous nature of the reaction of the potassium metal with BrF_3 , the cell contents were spattered upon the exposed surface of the ball in the Hills-McCanna valve. Later, during pump down procedures, the BrF_3 would be evaporated leaving behind what was probably the crystallized KF addition product or KBrF_4 . This material gradually built up on the surface of the ball until it prevented effective sealing of the valve and scored the Teflon seats. While this did not permit any atmospheric leakage (bonnet and stem seals prevented this) it did permit the body of the valve to fill with helium and thus made it difficult to pump out the reaction cell successfully with the rough vacuum system.

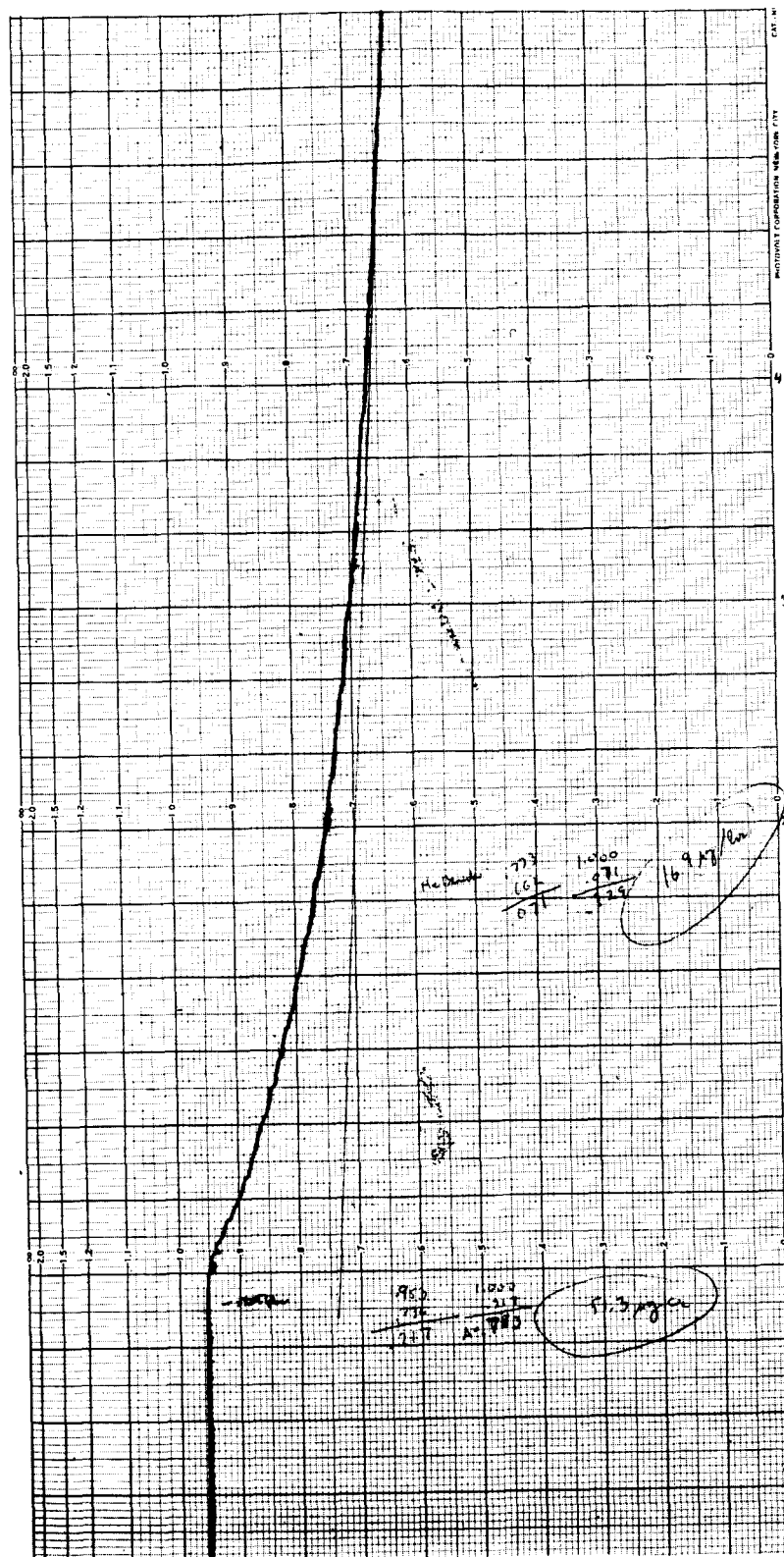


FIGURE 25 Typical Recorder Trace of Potassium Sample Containing 51.3 Micrograms of Oxygen

Since it was considered undesirable to pump large quantities of gas with the high vacuum system, owing to the presence of BrF_3 vapors, the system would then have to be cleaned out and the seals replaced. In this manner, a test of the amount of potassium which could be reacted with a given volume of BrF_3 was prevented. This difficulty might be overcome by substituting another type of valve, for example, a large plug valve, in place of the ball valve.

C. Oxygen Recovery from K_2CO_3 Additions

Other investigators⁽²⁾ have reported partial oxygen recovery from carbonates reacted with BrF_3 , but only under rather severe conditions. Sheft⁽⁹⁾ and co-workers attempted to ameliorate these conditions by using the KF and SbF_5 addition compounds of BrF_3 , which can be employed at temperatures up to 500°C without the disadvantages of high pressure. A 60 hour treatment of sodium carbonate with KBrF_4 at 500°C yielded only 74% oxygen. A similar treatment with the acid flux BrF_2SbF_6 yielded 100%. The difficulty in obtaining a complete reaction was attributed to the formation of a volatile intermediate, carbonyl difluoride, which did not remain in contact with the fluorinating agent for a sufficient length of time.

In view of the relatively mild conditions employed in our study and the fact that COF_2 , if formed, would be frozen out in the effluent cold traps (COF_2 m.p. -114°C); one would expect the oxygen recovery to be very low or even negligible. These expectations were borne out by the results which are listed in Table V.

The carbonate standards were made up in a manner analagous to that used for the bromate standards employing a standard solution containing 2.8794 grams of K_2CO_3 per liter. Since $\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ loses water at 130°C , the samples were heated at 170°C for two hours to insure dehydration. Under these conditions, the copper boats oxidized visibly; accordingly, 0.005" nickel sheet was used instead. The blanks for the nickel foil (16.0 micrograms O_2) were reproducible but higher than those obtained for copper during the bromate analyses. This

TABLE V

OXYGEN RECOVERY FROM K_2CO_3 ADDITIONS

<u>Oxygen Content</u> <u>(micrograms)</u>	<u>O₂ Recovered</u> <u>(micrograms)</u>
30	+ 5.3
60	- 0.6
90	- 8.8
90	+ 8.8
120	+ 9.8
$\Sigma = 390$	$\Sigma = + 1.3$

% Recovery = 0.33

may have been due to the pickling procedure used to clean the sheet prior to use. Instead of HF, which was employed in the case of the copper sheet, aqua regia was used.

The analytical procedure for the carbonate analyses was identical to that used for potassium samples and an apparatus blank of 7.3 micrograms was used in calculating the results.

The inference from this study is that if carbonate is present with oxide in the potassium only the oxygen from the latter is recorded by the BrF_3 procedure as used.

V CONCLUSIONS AND RECOMMENDATIONS

Oxygen values obtained by the BrF_3 method on potassium metal are reproducible, but higher than those obtained by mercury amalgamation. Comparative data between the BrF_3 and neutron activation methods is insufficient to resolve these differences. If, as has been postulated, the differences are due to the presence of thermodynamically stable binary or ternary oxide species which cannot be detected by mercury amalgamation, then the two methods may be regarded as complimentary rather than contradictory. No definitive evaluation of the bromine trifluoride method can be made until these differences are either explained or resolved.

Essentially complete oxygen recovery was obtained from potassium bromate additions; however, the results obtained from potassium carbonate additions indicate that oxygen present as carbonate is unrecovered. The possibility exists that the reaction yields a carbonyl fluoride (COF_2) that is trapped out.

The possibility exists that some unidentified reaction products may be passing through the effluent traps and is being measured as oxygen.

This possibility could be investigated in a number of ways including, of course, mass spectrometer studies.

There is no apparent reason why the BrF_3 method should not be applicable to sodium as well as potassium and only time limitations prevented the analysis of sodium samples. Lithium, NaK, and cesium present different sampling problems and some equipment modifications would be necessary in order to accommodate them. In addition, the much lower solubility of lithium fluoride in BrF_3 ($0.081 \pm .007$ gram moles per 100 grams of solution) and the reactivity of NaK or cesium would present additional but resolvable problems.

The application of the BrF_3 approach is pertinent for the analysis of oxygen in lithium. While the literature varies toward the applicability of the amalgamation or alkyl halide methods for other alkali metals, there appears to be common agreement that each (or other methods) is inadequate for lithium. With the increasing utility of lithium, the species obtained by interaction with BrF_3 is of positive interest. The work of Dupraw⁽⁵⁾ showed that nitrogen was liberated from titanium by bromine trifluoride and could be measured manometrically. The liberation of nitride nitrogen from lithium (as N_2 or NF_3) would be expected along with oxygen from this alkali metal.

A number of minor equipment modifications could be made in order to improve the performance of the existing apparatus and to facilitate future analytical needs. Replacement of the large ball valve by some other type less subject to seal damage has already been mentioned. Provisions could be made for cleaning out the reaction cell without disassembly or exposing the interior of the vessel to moisture or air. While this would, of course, necessitate rather complicated additions to the apparatus, the time spent in pre-fluorinating the equipment after each cleanout would be saved. A BrF_3 liquid level sensing device utilizing the rather high electrical conductivity of BrF_3 could also be placed in the reaction cell.

Before this method is applied to the analysis of more reactive alkali metals such as cesium, some thought should be given to the installation of safety equipment to handle excessive pressures, should they be encountered. This might consist simply of a safety tank connected to the reaction cell and separated from it by a monel rupture disk. Such safety precautions should also be considered if very large samples of potassium or sodium are to be run.

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